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Thermoelectric material comprising scandium doped zinc cadmium oxide

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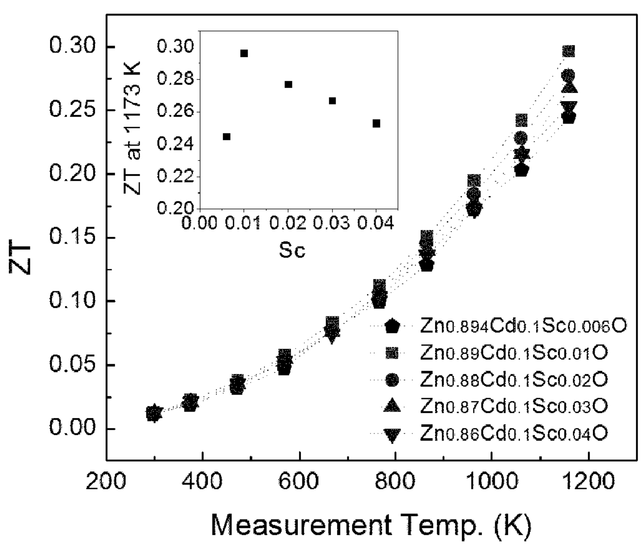
FIG. 9B



(57) Abstract: There is presented a composition of scandium doped Zinc Cadmium Oxide with the general formula $Zn_zCd_xSc_yO$ which the inventors have prepared, and for which material the inventors have made the insight that it is particularly advantageous as an n-type oxide material, such as particularly advantageous for high temperature thermoelectric application with good TE properties and superior stability in air. In a particular embodiment, there is presented a material with the general formula $Zn_{1-x-y}Cd_xSc_yO$, where $0.05<x<0.15$, $0.006<y<0.04$, which may have particularly advantageous values. Sc-doped Zn CdO is extremely robust in air at high temperatures up to 1173 K, and its TE performance is maintained after multiple heating and cooling cycles in air. So in short, the material is a new type of n-type material with superior properties for high temperature thermoelectric applications.

THERMOELECTRIC MATERIAL COMPRISING SCANDIUM DOPED ZINC CADMIUM OXIDE

FIELD OF THE INVENTION

The present invention relates to thermoelectric materials, more particularly n-type thermoelectric materials comprising scandium doped zinc cadmium oxide $Zn_ZCd_XSc_YO$ and a corresponding device comprising said n-type thermoelectric material, a method for preparing said n-type thermoelectric material and use of said n-type thermoelectric material.

BACKGROUND OF THE INVENTION

Thermoelectric (TE) technology is one of the most promising energy conversion technologies. It directly converts heat into electricity without any moving parts. Its superior reliability has made it a crucial long-life power sources for space needs since the 1950s. For civil use, thermoelectrics offers a promising solution for waste heat recovery. By integrating thermoelectric generators into many systems such as cars, fossil fuel power stations, and solar panels etc., the overall energy efficiency of the system can be improved. For industrial processes like those involving petroleum, steel manufacturing, transportation etc., there is an abundance of exploitable high temperature (such as above 500 K, such as 600-1200 K) waste heat. It calls for thermoelectric systems comprising high temperature stable materials with good thermoelectric properties, such as oxide thermoelectric materials, which may be efficient and stable over time, even at elevated temperatures, so as to enable reliably and efficiently converting thermal energy into electrical energy.

Hence, an improved thermoelectric material would be advantageous, and in particular a more stable and/or efficient thermoelectric material would be advantageous.

SUMMARY OF THE INVENTION

In particular, it may be seen as an object of the present invention to provide a more stable and/or efficient thermoelectric material.

It is a further object of the present invention to provide an alternative to the prior art.

Thus, the above described object and several other objects are intended to be obtained in a first aspect of the invention by providing an n-type thermoelectric material comprising scandium doped zinc cadmium oxide ($Zn_zCd_xSc_yO$), optionally comprising one or more further dopants.

The invention may be particularly, but not exclusively, advantageous for obtaining an n-type material with particularly beneficial properties, such as high ZT values and/or high stability, such as being particularly useful for high temperature thermoelectric applications. By high temperature may in general be understood more than 500 K, such as 600-1200 K. The material has been successfully synthesized and tested in the laboratory. The material shows very good properties suitable for high temperature thermoelectric application as an n-type thermoelectric material, and may for example be advantageous as n-type legs in a thermoelectric generator module.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, given by the formula $Zn_zCd_xSc_yO$, optionally comprising one or more further dopants, wherein

a. x is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
b. y is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
c. z is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001.

The values x, y, z, are to be understood as the amount of the element in the composition with respect to the amount of Zn in a ZnO composition. The values x and y may be referred to as the doping ratio or the doping fraction, corresponding to the ratio between the number $N_{\text{atoms of the dopant Cd}}$ and $N_{\text{atoms of the dopant Sc}}$ of, respectively, Cd and Sc, and the number $N_{\text{atoms of Zn in ZnO}}$ of Zn atoms in a corresponding ZnO composition, such as:

$$x = (N_{\text{atoms of the dopant Cd}})/(N_{\text{atoms of Zn in ZnO}})$$
$$y = (N_{\text{atoms of the dopant Sc}})/(N_{\text{atoms of Zn in ZnO}})$$

It is further to be understood, that where the amount scales from 0 (corresponding to the corresponding element not being present) to 1 (corresponding to all of the Zn in a corresponding ZnO material being replaced in the case of the sum of x and y being 1, or to all of the Zn still being present in the case of z being 1 correspondong to ZnO).

For example, if x is 0.1, it corresponds to a ZnO structure where every 10^{th} Zn atom in a corresponding ZnO material has been replaced with a Cd atom. If no other elements are present in the material, the Zn:Cd ratio is then 9:1. If other elements are present (as dopants instead of Zn), the Zn:Cd ratio is then below 9:1.

For example, if x is 0.1 and y is 0.01, it corresponds to a ZnO structure where every 10^{th} Zn atom in a corresponding ZnO material has been replaced with a Cd atom, and where every 100^{th} Zn atom in a corresponding ZnO material has been replaced with a Sc atom. If no other elements are present in the material, the Zn:Cd ratio is then 89:10 and the Zn:Sc ratio is 89:1 and the Cd:Sc ratio is x:y = 10:1. If other elements are present (as dopants instead of Zn), the Zn:Cd ratio is then below 89:1 and the Zn:Sc ratio is the below 89:1 but the Zn:Sc ratio remains x:y = 10:1.

By ‘optionally comprising one or more further dopants’ it may be understood that one or more further dopants may be present, such as the formula $Zn_zCd_xSc_yO$ implies the presence of the elements in the formula, but does not exclude the presence of other elements, such as one or more further dopants, such as Ga, Sn and/or Ce. Accordingly, the formula could be written $Zn_zCd_xSc_yA_wO$, where A corresponds to one or more optional dopants, such as Ga, Sn and/or Ce. The amount w may in embodiments be 0 (corresponding to no further dopants). The amount w may in embodiments be less than 0.5, such as less than 0.2, such as less than 0.1, such as less than 0.01, such as less than 0.001 (corresponding to no further dopants or a limited amount of further dopants).

By 'thermoelectric' may be understood a material, for which the thermoelectric effect renderst the material suitable for use as a thermoelectric material, e.g., in a thermoelectric generator module.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15,
- the value of y is equal to or larger than 0.001,
- the value of y is equal to or less than 0.05.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of y is equal to or larger than 0.006,
- the value of y is equal to or less than 0.04.

An possible advantage of adding scandium as a dopant, may be that the Sc dopants, such as within the range of 0.6 to 4 mol% (i.e., y within the range 0.006-0.04), may act as extrinsic donors, such as so as to provide the carrier concentration between $4.71\text{x}10^{19}$ cm^{-3} to $6.02\ \text{x}10^{19}$ cm^{-3}.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15.

An possible advantage of adding Cd into ZnO may be that it results in a decrease of the thermal conductivity, such as with minor affect of the electrical properties. It may be an advantage that x is equal to or larger than 0.05 since this may enable a pronounced effect to the thermal conductivity. It may be an advantage that x is equal to or less than 0.15 since this may enable avoiding too much degradation of electrical transport properties.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15
- the value of y is equal to or larger than 0.006,
- the value of y is equal to or less than 0.04.

A Scandium doped Zinc Cadmium Oxide (which may be interchangeably referred to as Sc-doped ZnCdO) with the general formula $Zn_{1-x-y}Cd_xSc_yO$, such as $Zn_{1-x-y}Cd_xSc_yO$, with 0.05<x<0.15, 0.006<y<0.04, which the inventors have prepared, and for which material the inventors have made the insight that it is particularly advantageous as an n-type oxide material, such as particularly advantageous for high temperature thermoelectric application with good TE properties and superior stability in air. Sc-doped ZnCdO has a significant low thermal conductivity (8.0 - 2.0 $W/m^{-1}K^{-1}$). Sc-doped ZnCdO also exhibits a rather low electrical resistivity (1.5×10^{-3} - 3.8×10^{-3} Ωcm) and good Seebeck coefficient (70 – 160 μV/K) in a wide temperature range from 300 K up to 1200 K, thus a large power factor is obtainable. The dimensionless figure-of-merit (ZT) that determines the conversion efficiency of a thermoelectric power generator is approximately 0.3 @1173 K and approximately 0.24 @1073 K, which are comparable or better to the state-of-the-art n-type thermoelectric oxide materials. Sc-doped ZnCdO is extremely robust in air at high temperatures up to 1173K, and its TE performance is maintained after multiple heating and cooling cycles in air. So in short, the material is a new type of n-type material with superior properties for high temperature thermoelectric applications.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15,
- the value of y is equal to or larger than 0.006,
- the value of y is equal to or less than 0.04,

and wherein z is within 0.810 and 0.944.

An advantage of this embodiment may be that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.06,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.001,
- the value of y is equal to or less than 0.05.

An advantage of this embodiment may be that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.08,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.001,
- the value of y is equal to or less than 0.05.

An advantage of this embodiment may be that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.08,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.002,
- the value of y is equal to or less than 0.04.

An advantage of this embodiment may be that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.08,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.005,

- the value of y is equal to or less than 0.04.

An advantage of this embodiment may be that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.08,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.005,
- the value of y is equal to or less than 0.025.

An advantage of this embodiment may be, that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.085,
- the value of x is equal to or less than 0.13,
- the value of y is equal to or larger than 0.005,
- the value of y is equal to or less than 0.025.

An advantage of this embodiment may be, that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein:

- the value of x is equal to or larger than 0.09,
- the value of x is equal to or less than 0.11,
- the value of y is equal to or larger than 0.008,
- the value of y is equal to or less than 0.012.

An advantage of this embodiment may be, that materials defined by these values may have relatively high ZT values.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the sum of x and y is less than unity and wherein z is within 0.50 and 1.0, such as within 0.80 and 0.949, such as within 0.810 and 0.944.

'Unity' is understood to correspond to the number 1 (one).

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the sum of x and y is less than unity and wherein z is substantially equal to 1-x-y, such as wherein z is equal to 1-x-y.

In an embodiment, there is presented an n-type thermoelectric material, wherein:

- the value of z is equal to or less than 1-x-y.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, consisting of the elements zinc, cadmium, scandium and oxygen, and optionally 1 or 2 further elements.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein z is 0.9, x is 0.1 and y is 0.01. An advantage of this embodiment may be that materials defined by these values may have a relatively high ZT value.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the n-type thermoelectric material is capable of maintaining a figure of merit above 0.20 when measured at 1173 K, such as above 0.25 when measured at 1173 K, such as above 0.26 when measured at 1173 K, such as above 0.27 when measured at 1173 K, such as above 0.275 when measured at 1173 K, after being kept for at least 1 hour, such as at least 10 hours, such as at least 25 hours, such as at least 50 hours, such as at least 100 hours, at a temperature of 1073 K in atmospheric air. A possible advantage of this may be that the material is stable (such as maintaining a high figure of merit, such as 0.20, such as 0.25, such as 0.26, such as 0.27, such as 0.275, when measured at 1173 K, even after being kept at a high temperature for extended periods of time, such as 1073 K for 1 hr or more) in air for long operation time, such as 1 hr or more, and at high temperature, such as up to 1073 K. This may in turn be seen as advantageous, in particular for thermoelectric materials, which are typically subjected to elevated temperatures during operation, since this enables that the efficiency stays relatively high even when operated at elevated temperatures. It may thus be seen as an advantage, that the material enables dispensing with a need for extra ambient protection.

'Figure of merit' is generally known in the fileld and in the present application used interchangeably with the 'ZT' value and the 'zT' value. Different from the effective device ZT, the material's figure of merit zT is a pure material property related to both electrical transport properties and thermal transport properties. It is given by the expression,

$$zT = (S^2\sigma/\kappa)T$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is temperature.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the n-type thermoelectric material is capable of maintaining a figure of merit above 90 % with respect to a starting value when measured at 1173 K, such as above 95 % when measured at 1173 K, such as above 97.5 % when measured at 1173 K, after being kept for at least 1 hour, such as at least 10 hours, such as at least 25 hours, such as at least 50 hours, such as at least 100 hours, at a temperature of 1073 K in atmospheric air. It may be understood that the starting value is given as a value being measured at 1173 K immediately before being exposed to a temperature of 1073 K in atmospheric air. A possible advantage of this may be that the material is stable (such as maintaining a high figure of merit, such decreasing less than 10 %, such as less than 5 %, such as less than 2.5 % when measured at 1173 K, after being kept at a high temperature for extended periods of time, such as 1073 K for 1 hr or more) in air for long operation time, such as 1 hr or more, and at high temperature, such as up to 1073 K.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the Figure of Merit (zT) when measured at a temperature of 1173 K is equal to or larger than 0.10, such as equal to or larger than 0.15, such as equal to or larger than 0.20, such as equal to or larger than 0.275.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein

a. the resistivity (ρ) when measured at room temperature (RT), such as when measured at 300 K, is equal to or less than $1x10^{-4}$ Ωm, such as equal to or less than $5x10^{-5}$ Ωm,

and/or

b. the resistivity (ρ) when measured at a temperature of 1173 K is equal to or less than $5x10^{-3}$ Ωm, such as equal to or less than $1x10^{-4}$ Ωm.

By room temperature may in general be understood 290-310 K, such as 300 K.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein the resistivity (ρ) when measured at a temperature of 1073 K is equal to or less than $5x10^{-4}$ Ωm after thermal cycling, said thermal cycling being in atmospheric air and comprising:

a. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,
b. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,
c. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,
d. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,
e. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,

such as equal to or less than $1x10^{-4}$ Ωm after said thermal cycling, such as equal to or less than $5x10^{-5}$ Ωm after said thermal cycling.

It may in general be seen as advantageous, if a thermoelectric material endures thermal cycling, since such material will typically be subjected to thermal cycling during operation, hence maintaining a high ZT value during thermal cycling, may typically yield the advantage that the ZT value is maintained at a high level during operation.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein

a. the numerical value of the Seebeck coefficient (S) at room temperature (RT), such as at 300 K, is equal to or larger than 30 μV/K, such as equal to or larger than 60 μV/K,

and/or

b. the numerical value of the Seebeck coefficient (S) at a temperature of 1173 K is equal to or larger than 75 μV/K, such as equal to or larger than 150 μV/K.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein

a. the Power Factor (PF) at room temperature (RT), such as at 300 K, is equal to or larger than 1.5 $\mu Wcm^{-1}K^{-2}$, such as equal to or larger than 2.5 $\mu Wcm^{-1}K^{-2}$.

and/or

b. the Power Factor (PF) at a temperature of 1173 K is equal to or larger than 3 $\mu Wcm^{-1}K^{-2}$, such as equal to or larger than 6 $\mu Wcm^{-1}K^{-2}$.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein

a. the thermal conductivity (κ) at room temperature (RT), such as at 300 K, is equal to or less than 15 $Wm^{-1}K^{-1}$, such as equal to or less than 8 $Wm^{-1}K^{-1}$

and/or

b. the thermal conductivity (κ) at a temperature of 1173 K is equal to or less than 6 $Wm^{-1}K^{-1}$, such as equal to or less than 3 $Wm^{-1}K^{-1}$.

In an embodiment, there is presented an n-type thermoelectric material comprising scandium doped zinc cadmium oxide, wherein a main phase of the material is having a hexagonal crystal structure, such as space group P63mc.

According to a second aspect, there is presented a device for interconversion between thermal energy and electric energy, said device comprising an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to the first aspect or any embodiment within the first aspect, such as the device being a thermoelectric generator. This aspect of the invention is particularly, but not exclusively, advantageous in that the device may be implemented by, e.g., as a thermoelectric generator module, which may be beneficial for interconversion between thermal energy and electric energy.

In an embodiment, the device may comprise a plurality of separate elements comprising the n-type thermoelectric material according to the first aspect, such as wherein said separate elements correspond to legs in a thermoelectric generator module.

In an embodiment, there is presented a device, such as a thermoelectric generator module, which comprises

- a plurality of separate elements, such as n-type legs, comprising the-type thermoelectric material according to the first aspect or any embodiment with the first aspect,
- a plurality of separate elements, such as p-type legs, comprising a p-type thermoelectric material.

The legs may be arranged so that during use (such as the thermoelectric generator module being placed in a temperature gradient), the thermoelectric legs are thermally in parallel and electrically in series.

According to a third aspect, the invention further relates to a method for preparing an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to the first aspect or any embodiment within the first aspect, said method comprising a conventional solid-state-reaction (SSR), such as a conventional solid-state-reaction from starting powders of ZnO, CdO, and Sc_2O_3. This aspect of the invention is particularly, but not exclusively, advantageous for providing the material according to the first aspect. The method may be seen as providing a repeatable, scalable, and/or easy way to provide the material.

According to a fourth aspect, the invention further relates to use of an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the first aspect or any embodiment within the first aspect or a device according to the second aspect or any embodiment within the second aspect for interconversion between thermal energy and electric energy, such as for generating electric energy from thermal energy. This aspect of the invention may for example be embodied by use of said material and/or device for converting waste heat into electrical energy.

The first, second, third and fourth aspect of the present invention may each be combined with any of the other aspects. These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

The n-type thermoelectric materials comprising scandium doped zinc cadmium oxide $Zn_zCd_xSc_yO$ and a corresponding device comprising said n-type thermoelectric material according to the invention will now be described in more detail with regard to the accompanying figures. The figures show one way of implementing the present invention and is not to be construed as being limiting to other possible embodiments falling within the scope of the attached claim set.

FIG. 1A shows XRD patterns for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples.
FIG. 1B shows refined unit cell volume of the predominant phase.
FIG. 2 shows SEM images for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples.
FIG. 3 shows SEM-EDS elementary mapping for a $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sample.
FIG. 4 shows temperature dependence of total thermal conductivity for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples.
FIG. 5 shows temperature dependence of lattice thermal conductivity of the samples.
FIG. 6 shows temperature dependence of electrical resistivity for samples.
FIG. 7 shows temperature dependence of power factor for samples.
FIG. 8 shows temperature dependence of Seebeck coefficients for samples.
FIG. 9A shows temperature dependence of ZT values for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples.
FIG. 9B shows temperature dependence of ZT values for $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (y = 0.006 to 0.04) samples.
FIG. 10 shows temperature dependence of ZT values for $Zn_{0.88}Cd_{0.1}A_{0.02}O$ (A = Sc, Ga, Sn, Ce) and $Zn_{0.88}Cd_{0.1}Sc_{0.01}B_{0.01}O$ (B = Mg, Sn, Ce) samples.
FIG. 11 shows photographs of the material an n-type thermoelectric material comprising scandium doped zinc cadmium oxide $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$.
FIG. 12 shows resistivity of $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ and $Zn_{0.98}Al_{0.02}O$ measured in air.
FIG. 13 shows time dependence of zT values, resistivity and Seebeck coefficient at 1173 K for $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sample after annealing in air at 1073 K.
FIG. 14 shows a device being a thermoelectric generator module.
FIG. 15 shows (a) a real picture of a sample measured in ULVAC-RIKO ZEM-3; (b) an illustrative scheme of the wire configuration with the sample for ULVAC-RIKO ZEM-3.

DETAILED DESCRIPTION OF AN EMBODIMENT

Material processing

Sc-doped ZnCdO can be obtained by e.g. a conventional solid-state-reaction (SSR) from the precursors of ZnO, CdO and Sc_2O_3. In the present example, the powders were mixed at the right molar ratio by roll milling using ceramic balls for 24 hr. Roll-mixing is an effective method for homogenizing the starting powder. The starting powder often consists of two or more than two component powders, for example ZnO, CdO and Sc_2O_3. First, the powders were weighed to the right amount and added together into a polyethylene bottle. Zirconia cylinders or balls were also added into the bottle as a mixing aid. Then the absolute ethanol with 1-2 wt% (weight percent) with respect to the powders was added. After that, the bottles were sealed and attached with the right safety labels. The mixing speed is 40 rpm and the time is for 24 hours. When the mixing procedure is finished, the resulting mixture was then uniaxially pressed with stainless steel die under 65 MPa for 60 seconds followed by isostatic pressing under 5 GPa for 60 seconds. The uniaxial pressing was using stainless steel dies with an inner diameter of 20 mm. About 6 to 8 grams of powder was added into the die and a pressing force of 18 kN (~2 Tons) was applied for 60 sec. The isostatic pressing was following the uniaxial pressing. The samples were first wrapped with an ultrasonic rubber bag, and then immerged into the isostatic pressing mould filled with water. A pressing force of 450 kN (~ 50 Tons) was applied for 60 sec. The green body was sintered in chamber furnace at 850 °C for 24 hr in air and then 1300 °C for 5 hr in air atmosphere to maintain the oxygen stoichiometry. The SSR method is using the conventional chamber furnace or tube furnace for sintering. The heating up and cooling down ramping rate was 300 K/h. More generally, doped Zinc Cadmium Oxide ($Zn_{1-x-y}Cd_xA_yO$, A = Sc, Ga, Ce, Mg, Sn etc.) may be obtained along a similar route from the starting powders of ZnO, CdO, Sc_2O_3, Ga_2O_3, Ce_2O_3, MgO, Sn_2O_3.

The sintered body reaches a relative density of approximately 96 %.

The sintered bulk material can then be cut with desired configurations and used for thermoelectric application.

For $Zn_{1-x-y}Cd_xSc_yO$ (x = 0.1, y = 0.02), the main crystalline structure of this material appears to be wurtzite belonging to the space group of P63mc, similar to pure ZnO, as shown in FIG. 1. The lattice constants for this material (in Ångstrøm) are a = 3.29 Å, c = 5.25 Å, different from those of ZnO (a = 3.25 Å and c = 5.2 Å).

The elementary distributions of Sc-doped ZnCdO are homogeneous like alloys as shown in FIG. 3.

Material characterization

Measurements of the properties of the material have been conducted. The electrical resistivity (ρ) and Seebeck coefficient (S) were measured simultaneously and on the same position on the sample using an ULVAC-RIKO ZEM-3 under a low pressure of helium atmosphere from room temperature up to 1173 K. A real picture of a sample measured in ZEM-3 and a corresponding illustrative scheme of the wire configuration are shown in FIG. 15A and FIG. 15B, respectively.Before the measurements for electrical conductivity and Seebeck coefficient, samples were cut into about 4×4×12 mm^3 rectangular shape. The Seebeck coefficient was obtained by fitting the slope of the voltage difference dV against the temperature difference dT measured by two thermocouples.

Hall measurement was carried out at room temperature by van der Pauw method with a superconducting magnet (measured up to 2 T). Samples were cut into about 5×5×1 mm^3 squared pellets with contacts at four corners. The van der Pauw method was used with a superconducting magnet (5.08 T).

The thermal conductivity (κ) was determined from the thermal diffusivity (α), the mass density (D_m) and the specific heat capacity (C_p) according to the equation $\kappa = \alpha D_m C_p$. The thermal diffusivity was obtained by the laser flash method (Netzsch LFA-457, Germany), the mass densities of the samples were measured by Archimedes' method using water with surfactant, and the specific heat capacities were estimated using Dulong-Petit law. X-ray diffraction (XRD) pattern to examine the phase purity of the materials was obtained using a Bruker D8 diffractometer (Bruker, Germany) with Cu-Kα radiation. The phases were analyzed and identified with EVA software and the XRD refinements were performed using TOPAS software. A scanning electron microscope (SEM, Supra; Carl Zeiss, Inc., Germany) was used to observe the microstructures of the samples.

FIG. 1(a) shows The XRD patterns for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (where x from bottom to top is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples. For $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples, the main crystalline structure of this material is wurtzite belonging to the space group of P63mc, similar to pure ZnO, as shown in FIG. 1(a). For samples with x = 0.15 and 0.125, the secondary phase be observed by the peaks marked with '*' in FIG. 1(a). Those peaks are identical to those peaks of pure CdO. It indicates that once the molar ratio of CdO and ZnO exceeds 1:9, the excess CdO phase could not fully incorporate into the ZnO under our sintering conditions discussed above. When the ratio is below 1:9, CdO can very well incorporate with wurtzite ZnO phase. For samples with x = 0, 0.05 and 0.1, the Sc_2O_3 phase belonging to I213 space group can be observed by a weak peak marked with 'o ' in FIG. 1(a).

FIG. 1B shows refined unit cell volume of the predominant phase plotted as a function of Cd composition. By 'predominant phase' may be understood, a phase which occupies at least 80 wt%, such as at least 90 wt%, such as at least 95wt%, such as at least 99 wt%.

Similar XRD of samples with different amount of Sc keeping the amount of Cd constant at 0.1 have been obtained (not shown). For $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (y = 0 to 0.04) samples, the main crystalline structure of this material is the wurtzite which is belonging to the space group of P63mc. For samples with y = 0.02, 0.03 and 0.04, the Sc_2O_3 phase belonging to I213 space group can be observed by weak peaks marked. As the Cd concentration increases, the unit cell volumes remains almost constant with very slight changes.

FIG. 2 shows Scanning Electron Microscope (SEM) images for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (x = 0 to 0.15) samples. The subfigures show (a) x = 0.05, (b) x = 0.1, (c) x = 0.125, and (d) x = 0.15.

All the samples shown in FIG. 2 appear to be dense and with micron size grains. The grain sizes varied from ca. 4 μm to ca. 25 μm. The addition of CdO into ZnO improved the sample sintering and for a value of x = 0.1 of Cd resulted in the largest grain sizes of up to ca. 25 μm. Further addition of CdO caused the phase separation and thus changed the microstructure and resulted in smaller grains.

Similar SEM images of $Zn_{0.9-y}Cd_{0.1}Sc_{y}O$ (y = 0.01 to 0.04) samples have been obtained (not shown). The samples are dense, with micron size grains. The grain sizes of the samples for y = 0.01 and 0.02 are similar at about 25 μm. When the concentration of Sc exceeded 2 at%, the grains became smaller (to ~5 to 10 um) and pores of approximately ~1 μm appeared at grain boundaries, as seen for y = 0.03 and 0.04.

To verify the homogeneity and incorporation of Cd with ZnO, a SEM-EDS elemental mapping was performed on the sample $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$. As shown in FIG. 3, the distribution of Cd and Sc in ZnO are both uniform at the grain interiors, and there is also evidence of Zn deficiency at the grain boundaries. These observations are consistent with the information observed from the X-ray diffraction patterns. The CdO and ZnO incorporated with each other and formed oxide alloys. The excessive CdO could enrich at the grain boundaries and can be detected by XRD when Cd concentration is larger than corresponding to a value of x = 0.1.

FIG. 3 shows (in subfigures b-d) SEM Energy-dispersive X-ray spectroscopy (EDS) elementary mapping for a $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sample from which it can be seen that the material is homogeneous. The subfigure (a) is a SEM image, which correspond to the subfigure 2(b). The remaining subfigures show (b) elementary mapping of Zn, (c) elementary mapping of Cd, and (d) elementary mapping of Sc (the scalebar shows 6 micrometer). The scaling in all the FIG. 3 subfigures is similar.

FIG. 4 shows temperature dependence of total thermal conductivity for $Zn_{0.98-x}Cd_{x}Sc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples.

FIG. 5 shows temperature dependence of lattice thermal conductivity of the $Zn_{0.98-x}Cd_{x}Sc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples. The solid colour lines are the calculated values using the Debye-Callaway model.

FIG. 6A shows temperature dependence of electrical resistivity for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples.

FIG. 6B shows temperature dependence of electrical resistivity for $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (where y is given by: y = {0.006; 0.01; 0.02; 0.03; 0.04}) samples.

FIG. 6C shows temperature dependence of electrical resistivity for $Zn_{0.88}Cd_{0.1}A_{0.02}O$ (A = Sc, Ga, Sn, Ce) and $Zn_{0.88}Cd_{0.1}Sc_{0.01}B_{0.01}O$ (B = Mg, Sn, Ce) samples.

FIG. 7A shows temperature dependence of power factor for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples.

FIG. 7B shows temperature dependence of power factor for $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (where y is given by: y = {0.006; 0.01; 0.02; 0.03; 0.04}) samples.

FIG. 7C shows temperature dependence of power factor for $Zn_{0.88}$ $Cd_{0.1}A_{0.02}O$ (A = Sc, Ga, Sn, Ce) and $Zn_{0.88}$ $Cd_{0.1}Sc_{0.01}B_{0.01}O$ (B = Mg, Sn, Ce) samples.

FIG. 8 shows temperature dependence of Seebeck coefficient. All samples showed negative S values indicating again n-type conduction.

FIG. 8A shows temperature dependence of Seebeck coefficient for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples.

FIG. 8B shows temperature dependence of Seebeck coefficient for $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (where y is given by: y = {0.006; 0.01; 0.02; 0.03; 0.04}) samples.

FIG. 9A shows temperature dependence of ZT values for $Zn_{0.98-x}Cd_xSc_{0.02}O$ (where x is given by: x = {0; 0.05; 0.10; 0.125; 0.15}) samples. The inset shows the ZT value as measured at a temperature of 1173 K plotted as a function of x, i.e., plotted as a function of Cd content. It can be seen, that a maximum (0.3 @ 1173 K) is obtained for the value at x = 0.1.

FIG. 9B shows temperature dependence of ZT values for $Zn_{0.9-y}Cd_{0.1}Sc_yO$ (where y is given by: y = {0.006; 0.01; 0.02; 0.03; 0.04}) samples. It can be seen, that a maximum is obtained for the value at y = 0.01, which is slightly higher than the neighbouring value at y = 0.02 where a ZT value of 0.28 @ 1173 K is measured.

FIG. 10 shows temperature dependence of ZT values for $Zn_{0.88}Cd_{0.1}A_{0.02}O$ (A = Sc, Ga, Sn, Ce) and $Zn_{0.88}Cd_{0.1}Sc_{0.01}B_{0.01}O$ (B = Mg, Sn, Ce) samples. It can be seen, that a maximum is obtained for the value at A = Sc.

FIG. 11 shows photographs of the material an n-type thermoelectric material comprising scandium doped zinc cadmium oxide $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$. FIGS. 11(a)-(c) show typical sintered disc shaped sample and rectangular bars for thermoelectric module fabrication. More particularly, the subfigures show (a) a bulk pellet 1102 of $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sintered in air, (b) a pre-annealing rectangular segment 1104 cut from the bulk pellet 1102 of $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$, where the rectangular segment 1104 is held by a tweezer 1108, (c) a post-annealed rectangular segment 1106 of $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ corresponding to the pre-annealing rectangular segment 1104 after annealing in air at 1073 K for 72 hr.

It is a proof of the thermal stability of the material, that the $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sample sintered in air remained its dark greenish colour after annealing in air at 1073K for 72h (cf., FIGS. 11(b) and 11(c)), i.e., that the colour of the pre-annealing rectangular segment 1104 substantially corresponds to the post-annealed rectangular segment 1106.

In FIG. 11(a) the diameter of the bulk pellet 1102 is 25.4 mm. However, it is also conceivable that the diameter could be 10 times larger, such as 100 times larger, or that the diameter is 10 times smaller, such as 100 time smaller.

The segments shown in FIGS. 11(b) and 11(c) may be particularly useful as legs in a thermoelectric generator module.

The n-type thermoelectric material comprising scandium doped zinc cadmium oxide has isotropic properties. This may be seen as advantageous, since this may enable easier post-processing, such as processing of the material for practical applications.

It is noticeable, that Sc-doped ZnCdO not only has the high ZT values comparable, but more importantly has much better long-term stability in air, such as long-term stability up to temperatures of about 1173 K, where the other material, e.g. AZO, is not suitable due to degradation.

FIG. 12 shows resistivity of $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ and $Zn_{0.98}Al_{0.02}O$ measured in air during thermal cycling. It is particularly noticeable, that the resistivity of the $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ remains substantially constant during the thermal cycling (even at elevated temperatures above 1000 K), whereas the resistivity of the $ZnAl_{0.02}O$ material increases during the thermal cycle.

The long-term stability for Sc-doped ZnCdO was tested by annealing the sample in air at 1073 K for up to 100 hours. The ZT values for $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ after the annealing were recorded as shown in Fig. 13.

FIG. 13 shows time dependence of zT values, resistivity and Seebeck coefficient at 1173 K for $Zn_{0.88}Cd_{0.1}Sc_{0.02}O$ sample after annealing in air at 1073 K. It is noticed, that the degradation in terms of the zT value was approximately 2 % after 100 hours of annealing in air at 1073 K.

FIG. 14 shows a device being a thermoelectric generator module, which comprises

- a plurality of separate elements comprising the-type thermoelectric material according to the first aspect, such as n-type legs,
- a plurality of separate elements comprising a p-type thermoelectric material, such as p-type legs.

FIG. 15A shows a real picture of a sample measured in ULVAC-RIKO ZEM-3;

FIG. 15B shows an illustrative scheme of the wire configuration with the sample for ULVAC-RIKO ZEM-3 (corresponding to the picture in FIG. 15A). The scheme comprises upper ceramic tube 1110a, lower ceramic tube 1110b, upper metal wire 1112a, lower metal wire 1112b, a heater 1114, upper electrode 1114a, lower electrode 1114b (both of the upper and lower electrodes being Ni electrodes), the sample 1116, upper thermocouple 1118a and lower thermocouple 1118b.

To sum up, there is presented a composition of scandium doped Zinc Cadmium Oxide with the general formula $Zn_zCd_xSc_yO$ which the inventors have prepared, and for which material the inventors have made the insight that it is particularly advantageous as an n-type oxide material, such as particularly advantageous for high temperature thermoelectric application with good TE properties and superior stability in air. In a particular embodiment, there is presented a material with the general formula $Zn_{1-x-y}Cd_xSc_yO$, where $0.05<x<0.15$, $0.006<y<0.04$, which may have particularly advantageous values. Sc-doped ZnCdO is robust in air at high temperatures up to 1173K, and its TE performance is maintained after multiple heating and cooling cycles in air. So in short, the material is a new type of n-type material with superior properties for high temperature thermoelectric applications.

In alternative embodiments E1-E15, there is presented:

E1. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide ($Zn_zCd_xSc_yO$), optionally comprising one or more further dopants.

E2. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, given by the formula $Zn_zCd_xSc_yO$, optionally comprising one or more further dopants, wherein

a. x is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
b. y is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
c. z is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001.

E3. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein:

- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15,
- the value of y is equal to or larger than 0.001,
- the value of y is equal to or less than 0.05.

E4. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein:
- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15
- the value of y is equal to or larger than 0.006,
- the value of y is equal to or less than 0.04.

E5. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein:
- the value of x is equal to or larger than 0.05,
- the value of x is equal to or less than 0.15,
- the value of y is equal to or larger than 0.006,
- the value of y is equal to or less than 0.04,

and wherein z is within 0.810 and 0.944.

E6. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein:
- the value of x is equal to or larger than 0.08,
- the value of x is equal to or less than 0.14,
- the value of y is equal to or larger than 0.001,
- the value of y is equal to or less than 0.05.

E7. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein:
- the value of x is equal to or larger than 0.085,
- the value of x is equal to or less than 0.13,

- the value of y is equal to or larger than 0.005,
- the value of y is equal to or less than 0.025.

E8. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein the sum of x and y is less than unity and wherein z is within 0.50 and 1.0, such as within 0.80 and 0.949, such as within 0.810 and 0.944.

E9. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein z is 0.89, x is 0.1 and y is 0.01.

E10. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein the n-type thermoelectric material is capable of maintaining a figure of merit above 0.20 when measured at 1173 K, such as above 0.25 when measured at 1173 K, after being kept for at least 1 hour, such as at least 10 hours, such as at least 25 hours, such as at least 50 hours, such as at least 100 hours, at a temperature of 1073 K in atmospheric air.

E11. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein the Figure of Merit (zT) when measured at a temperature of 1173 K is equal to or larger than 0.10, such as equal to or larger than 0.15, such as equal to or larger than 0.20, such as equal to or larger than 0.275.

E12. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, wherein the resistivity (ρ) when measured at a temperature of 1073 K is equal to or less than 5×10^{-4} Ωm after thermal cycling, said thermal cycling being in atmospheric air and comprising:

a. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,
b. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,

c. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,

d. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,

e. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,

such as equal to or less than $1x10^{-4}$ Ωm after said thermal cycling, such as equal to or less than $5x10^{-5}$ Ωm after said thermal cycling.

E13. A device for interconversion between thermal energy and electric energy, said device comprising an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding embodiments, such as the device being a thermoelectric generator.

E14. A method for preparing an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of embodiments E1-E12, said method comprising a conventional solid-state-reaction (SSR), such as a conventional solid-state-reaction from starting powders of ZnO, CdO, and Sc_2O_3.

E15. Use of an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of embodiments E1-E12 or a device according to embodiment E13 for interconversion between thermal energy and electric energy, such as for generating electric energy from thermal energy.

For the above embodiments E1-E15, it may be understood that reference to preceding 'embodiments' may refer to preceding embodiments within embodiments E1-E15.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or “comprises” do not exclude other possible elements or steps. Also, the mentioning of references such as “a” or “an” etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in different claims does not exclude that a combination of features is not possible and advantageous.

CLAIMS

1. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide ($Zn_zCd_xSc_yO$), given by the formula $Zn_zCd_xSc_yO$, optionally comprising one or more further dopants, wherein
    a. x is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
    b. y is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001,
    c. z is larger than zero, such as larger than 0.000001, such as larger than 0.00001, such as larger than 0.001.

2. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein:
    - the value of x is equal to or larger than 0.05,
    - the value of x is equal to or less than 0.15,
    - the value of y is equal to or larger than 0.001,
    - the value of y is equal to or less than 0.05.

3. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein:
    - the value of x is equal to or larger than 0.05,
    - the value of x is equal to or less than 0.15
    - the value of y is equal to or larger than 0.006,
    - the value of y is equal to or less than 0.04.

4. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein:
    - the value of x is equal to or larger than 0.05,
    - the value of x is equal to or less than 0.15,
    - the value of y is equal to or larger than 0.006,
    - the value of y is equal to or less than 0.04,

    and wherein z is within 0.810 and 0.944.

5. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein:
   - the value of x is equal to or larger than 0.08,
   - the value of x is equal to or less than 0.14,
   - the value of y is equal to or larger than 0.001,
   - the value of y is equal to or less than 0.05.

6. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein:
   - the value of x is equal to or larger than 0.085,
   - the value of x is equal to or less than 0.13,
   - the value of y is equal to or larger than 0.005,
   - the value of y is equal to or less than 0.025.

7. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein the sum of x and y is less than unity and wherein z is within 0.50 and 1.0, such as within 0.80 and 0.949, such as within 0.810 and 0.944.

8. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein z is 0.89, x is 0.1 and y is 0.01.

9. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein the n-type thermoelectric material is capable of maintaining a figure of merit above 0.20 when measured at 1173 K, such as above 0.25 when measured at 1173 K, after being kept for at least 1 hour, such as at least 10 hours, such as at least 25 hours, such as at least 50 hours, such as at least 100 hours, at a temperature of 1073 K in atmospheric air.

10. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein the Figure of Merit (zT) when measured at a temperature of 1173 K is equal to

or larger than 0.10, such as equal to or larger than 0.15, such as equal to or larger than 0.20, such as equal to or larger than 0.275.

11. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein the resistivity (ρ) when measured at a temperature of 1073 K is equal to or less than 5×10^{-4} Ωm after thermal cycling, said thermal cycling being in atmospheric air and comprising:
    a. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,
    b. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,
    c. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,
    d. Decreasing the temperature from 1073 K to 300 K at a rate of 100 K/hr,
    e. Increasing the temperature from 300 K to 1073 K at a rate of 100 K/hr,

    such as equal to or less than 1×10^{-4} Ωm after said thermal cycling, such as equal to or less than 5×10^{-5} Ωm after said thermal cycling.

12. An n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, wherein the value of z is equal to or less than 1-x-y.

13. A device for interconversion between thermal energy and electric energy, said device comprising an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of the preceding claims, such as the device being a thermoelectric generator.

14. A method for preparing an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of claims 1-12, said method comprising a conventional solid-state-reaction (SSR), such as a conventional solid-state-reaction from starting powders of ZnO, CdO, and Sc_2O_3.

15. Use of an n-type thermoelectric material comprising scandium doped zinc cadmium oxide according to any one of claims 1-12 or a device according to claim 13 for interconversion between thermal energy and electric energy, such as for generating electric energy from thermal energy.

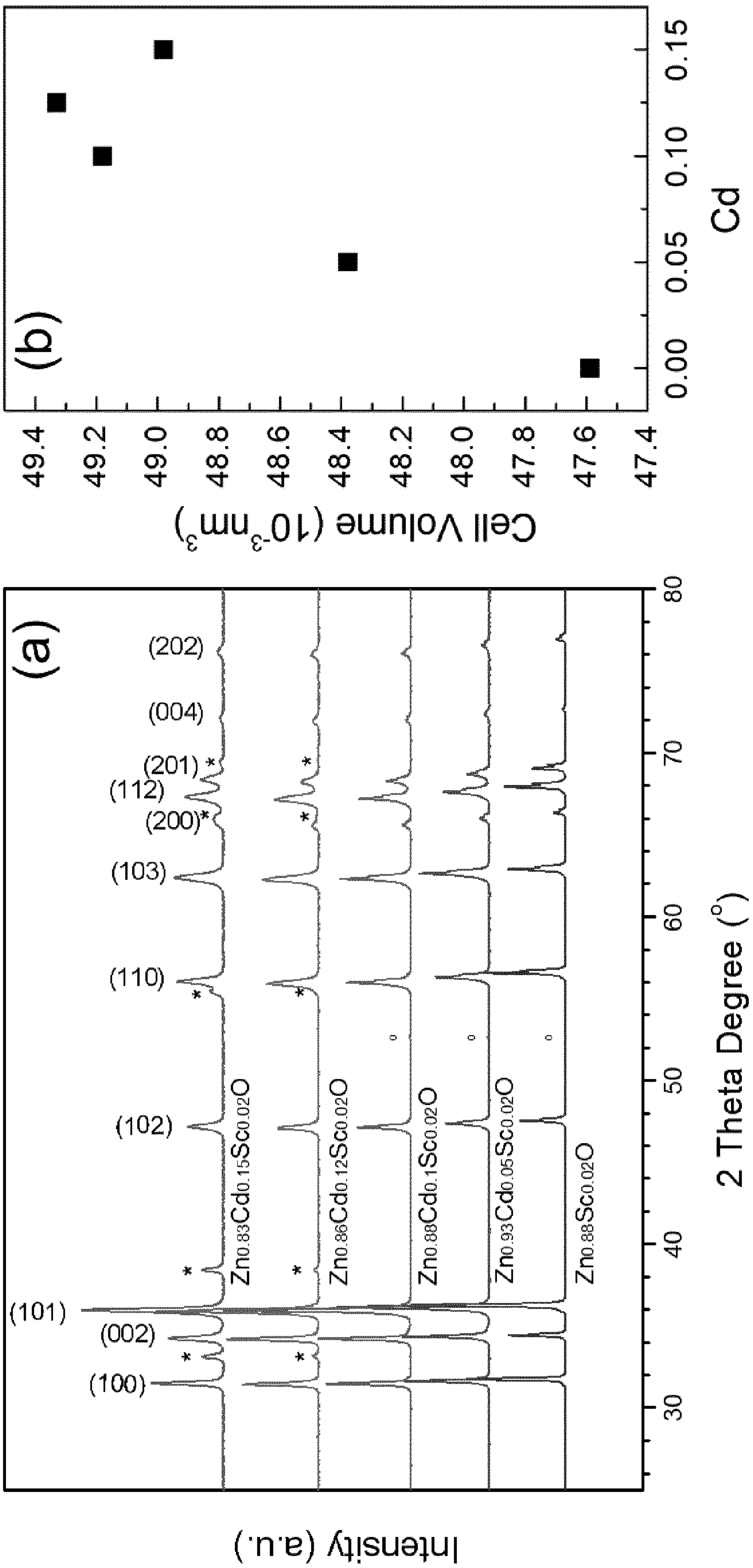

(a)
(b)
Cell Volume ($10^{-3}nm^3$)
Cd
0.00
0.05
0.10
0.15
49.4
49.2
49.0
48.8
48.6
48.4
48.2
48.0
47.8
47.6
47.4
Intensity (a.u.)
2 Theta Degree (°)
30
40
50
60
70
80
(100)
(002)
(101)
(102)
(110)
(103)
(200)*
(112)
(201) *
(004)
(202)
$Zn_{0.83}Cd_{0.15}Sc_{0.02}O$
$Zn_{0.86}Cd_{0.12}Sc_{0.02}O$
$Zn_{0.88}Cd_{0.1}Sc_{0.02}O$
$Zn_{0.93}Cd_{0.05}Sc_{0.02}O$
$Zn_{0.88}Sc_{0.02}O$

FIG. 1

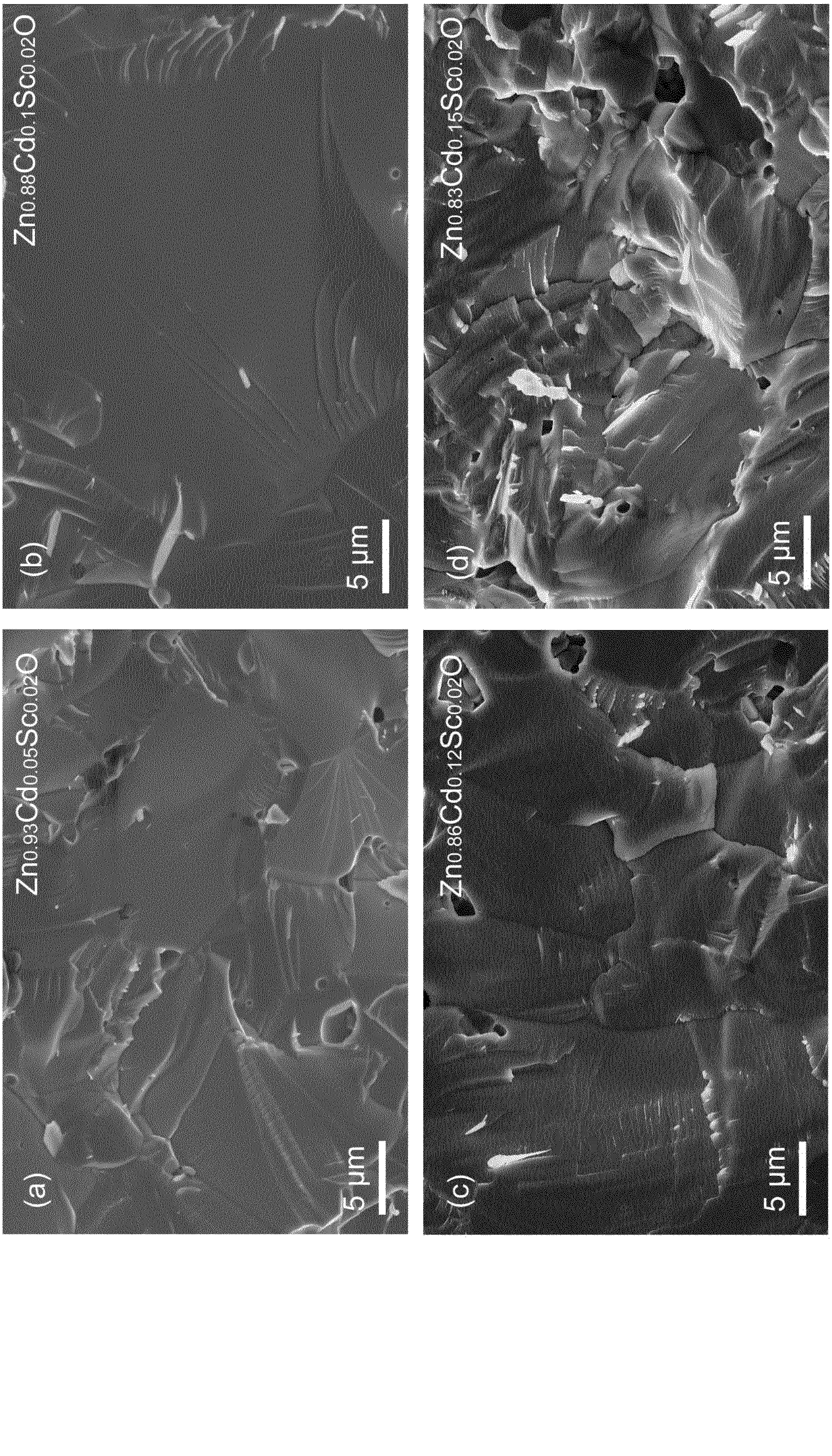

(a)
$Zn_{0.93}Cd_{0.05}Sc_{0.02}O$
5 µm
(b)
$Zn_{0.88}Cd_{0.1}Sc_{0.02}O$
5 µm
(c)
$Zn_{0.86}Cd_{0.12}Sc_{0.02}O$
5 µm
(d)
$Zn_{0.83}Cd_{0.15}Sc_{0.02}O$
5 µm

FIG. 2

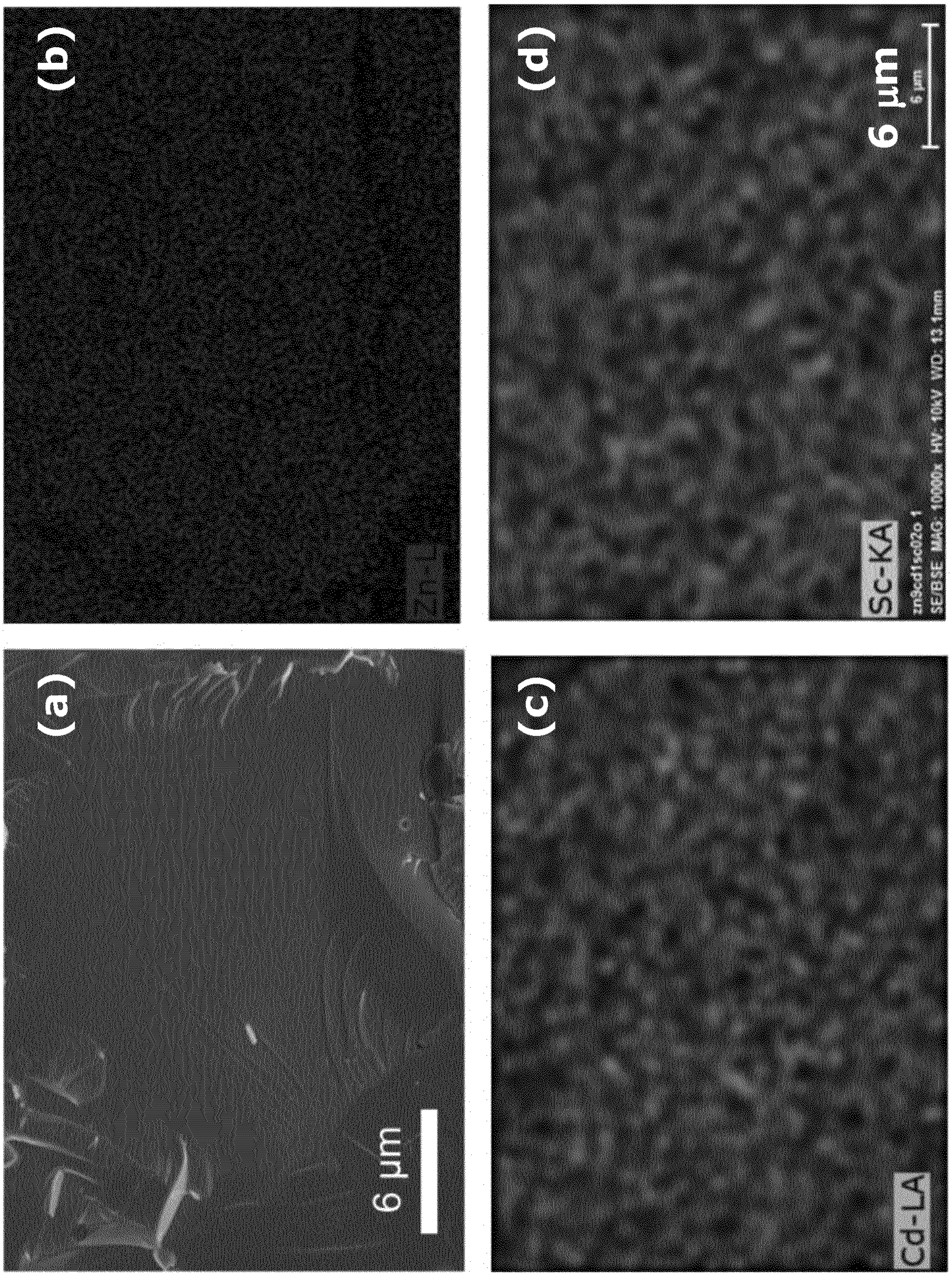


FIG. 3

FIG. 4

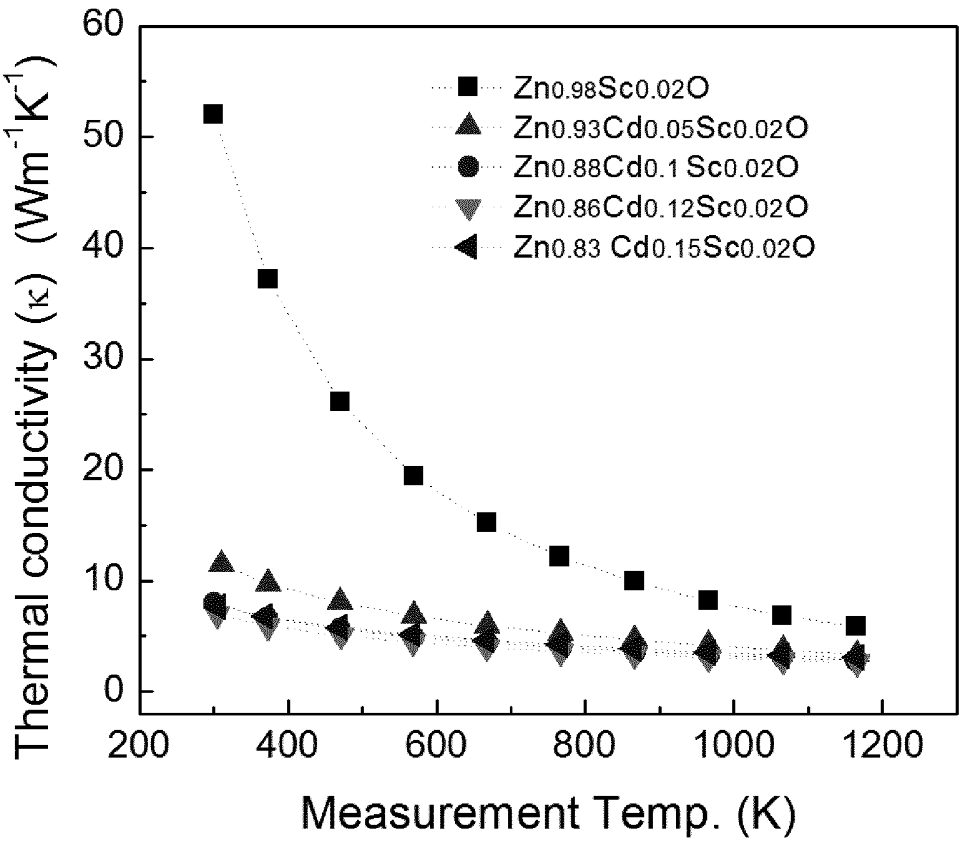

Thermal conductivity (κ) (Wm⁻¹K⁻¹)
Measurement Temp. (K)
Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83 Cd0.15Sc0.02O
0
10
20
30
40
50
60
200
400
600
800
1000
1200

FIG. 5

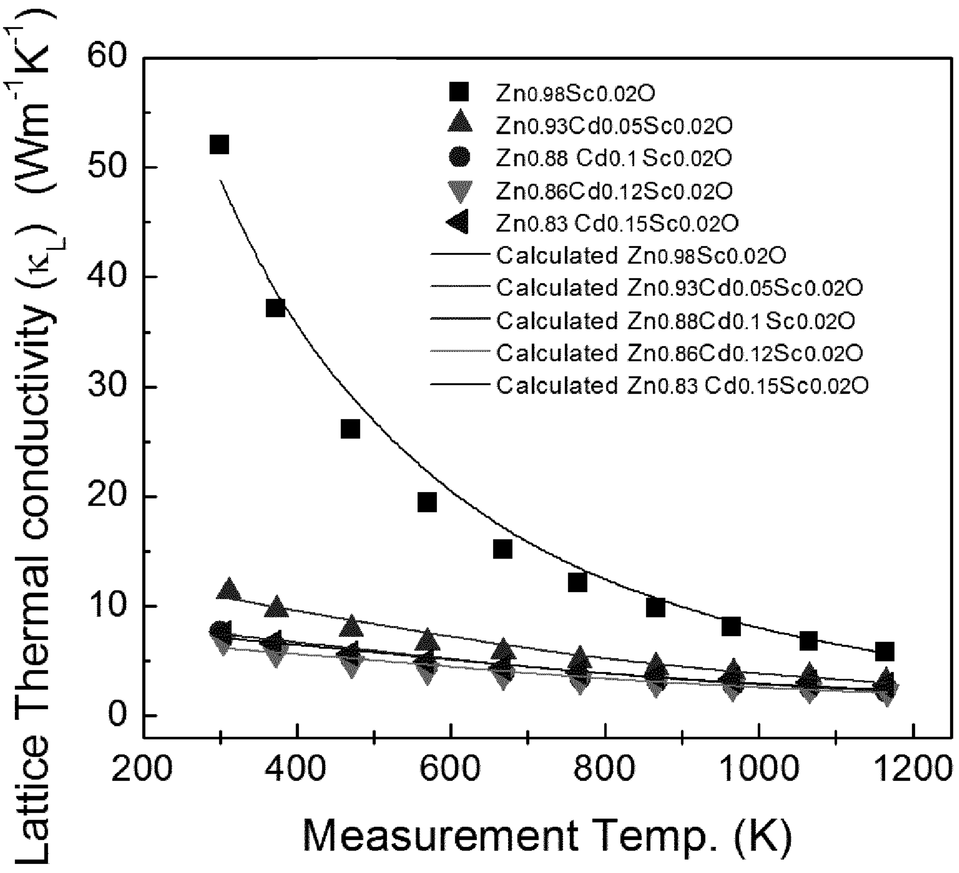

Lattice Thermal conductivity (κL) (Wm⁻¹K⁻¹)
Measurement Temp. (K)
Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88 Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83 Cd0.15Sc0.02O
Calculated Zn0.98Sc0.02O
Calculated Zn0.93Cd0.05Sc0.02O
Calculated Zn0.88Cd0.1 Sc0.02O
Calculated Zn0.86Cd0.12Sc0.02O
Calculated Zn0.83 Cd0.15Sc0.02O
0
10
20
30
40
50
60
200
400
600
800
1000
1200

FIG. 6A

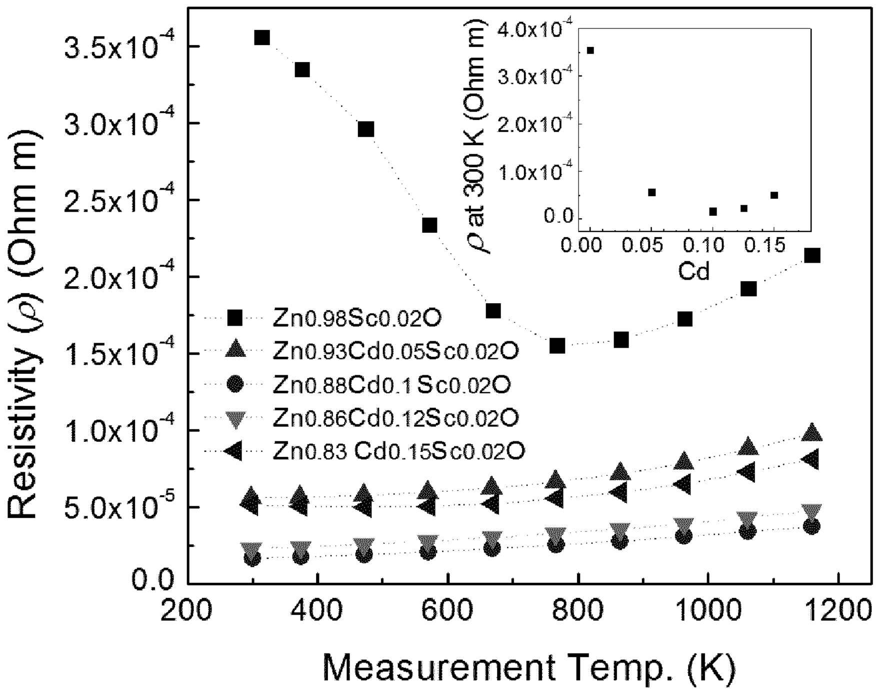
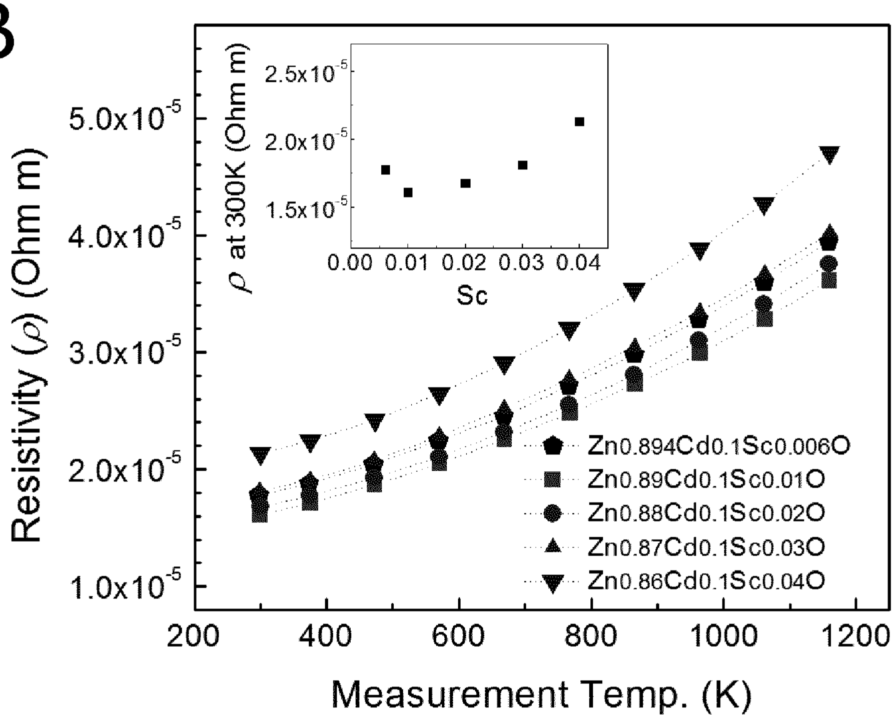

3.5x10^-4
3.0x10^-4
2.5x10^-4
2.0x10^-4
1.5x10^-4
1.0x10^-4
5.0x10^-5
0.0
Resistivity (ρ) (Ohm m)
200
400
600
800
1000
1200
Measurement Temp. (K)
Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83 Cd0.15Sc0.02O
4.0x10^-4
3.0x10^-4
2.0x10^-4
1.0x10^-4
0.0
ρ at 300 K (Ohm m)
0.00 0.05 0.10 0.15
Cd

FIG. 6B


5.0x10^-5
4.0x10^-5
3.0x10^-5
2.0x10^-5
1.0x10^-5
Resistivity (ρ) (Ohm m)
200
400
600
800
1000
1200
Measurement Temp. (K)
Zn0.894Cd0.1Sc0.006O
Zn0.89Cd0.1Sc0.01O
Zn0.88Cd0.1Sc0.02O
Zn0.87Cd0.1Sc0.03O
Zn0.86Cd0.1Sc0.04O
2.5x10^-5
2.0x10^-5
1.5x10^-5
ρ at 300K (Ohm m)
0.00 0.01 0.02 0.03 0.04
Sc

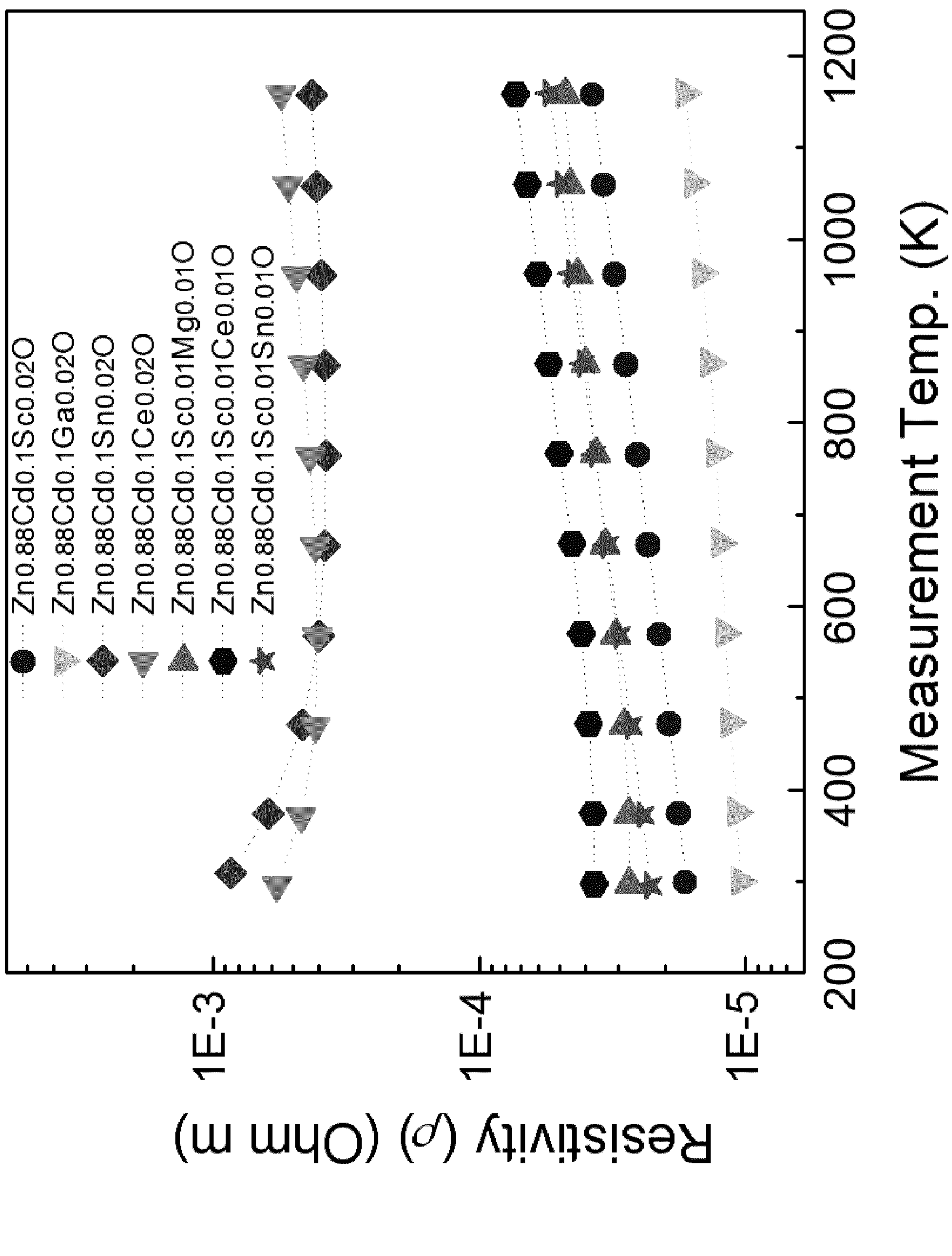

Zn0.88Cd0.1Sc0.02O
Zn0.88Cd0.1Ga0.02O
Zn0.88Cd0.1Sn0.02O
Zn0.88Cd0.1Ce0.02O
Zn0.88Cd0.1Sc0.01Mg0.01O
Zn0.88Cd0.1Sc0.01Ce0.01O
Zn0.88Cd0.1Sc0.01Sn0.01O
Resistivity (ρ) (Ohm m)
1E-3
1E-4
1E-5
200
400
600
800
1000
1200
Measurement Temp. (K)

FIG. 6C

FIG. 7A

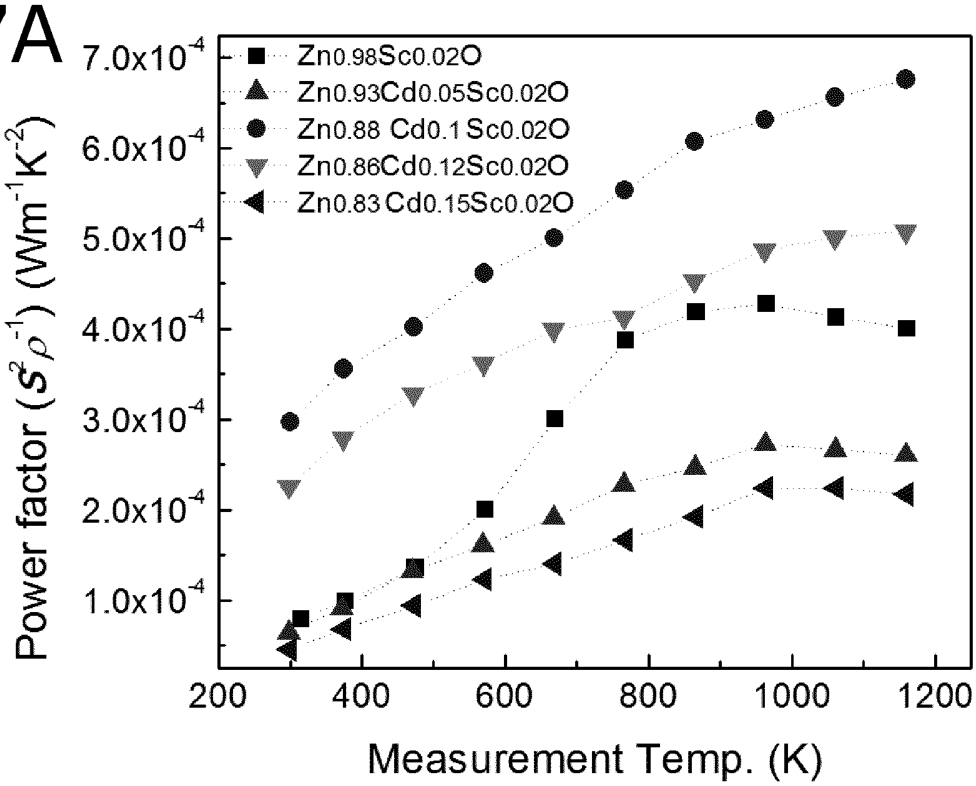
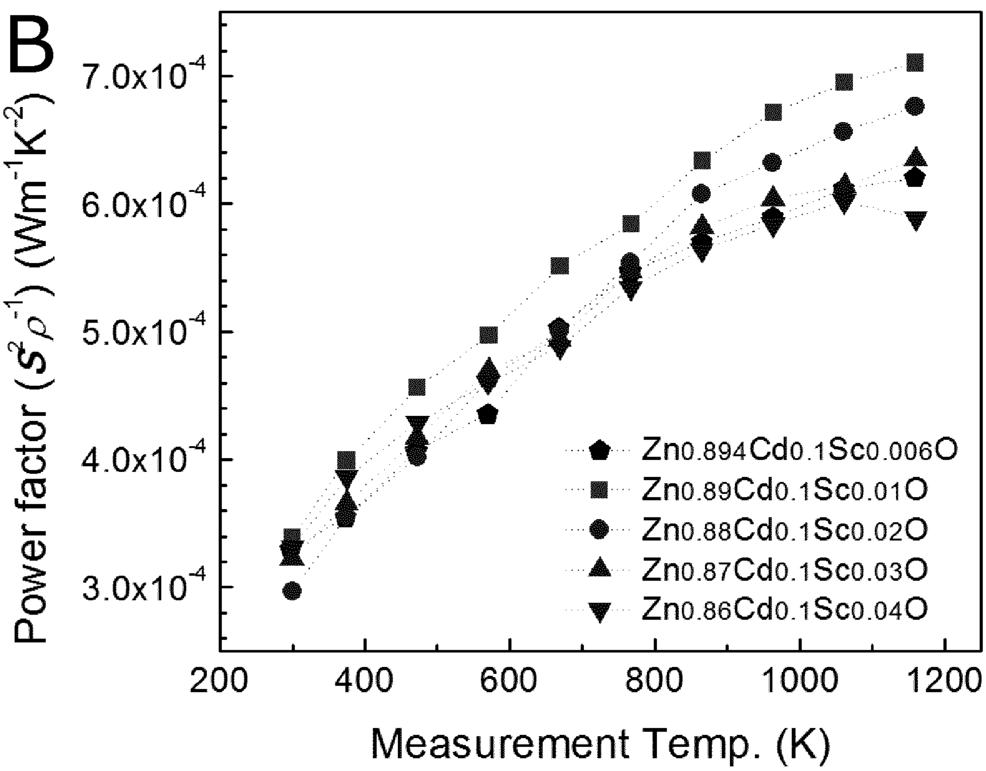

Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88 Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83 Cd0.15Sc0.02O
Power factor ($s^2\rho^{-1}$) ($Wm^{-1}K^{-2}$)
7.0x10^-4
6.0x10^-4
5.0x10^-4
4.0x10^-4
3.0x10^-4
2.0x10^-4
1.0x10^-4
200
400
600
800
1000
1200
Measurement Temp. (K)

FIG. 7B


Zn0.894Cd0.1Sc0.006O
Zn0.89Cd0.1Sc0.01O
Zn0.88Cd0.1Sc0.02O
Zn0.87Cd0.1Sc0.03O
Zn0.86Cd0.1Sc0.04O
Power factor ($s^2\rho^{-1}$) ($Wm^{-1}K^{-2}$)
7.0x10^-4
6.0x10^-4
5.0x10^-4
4.0x10^-4
3.0x10^-4
200
400
600
800
1000
1200
Measurement Temp. (K)

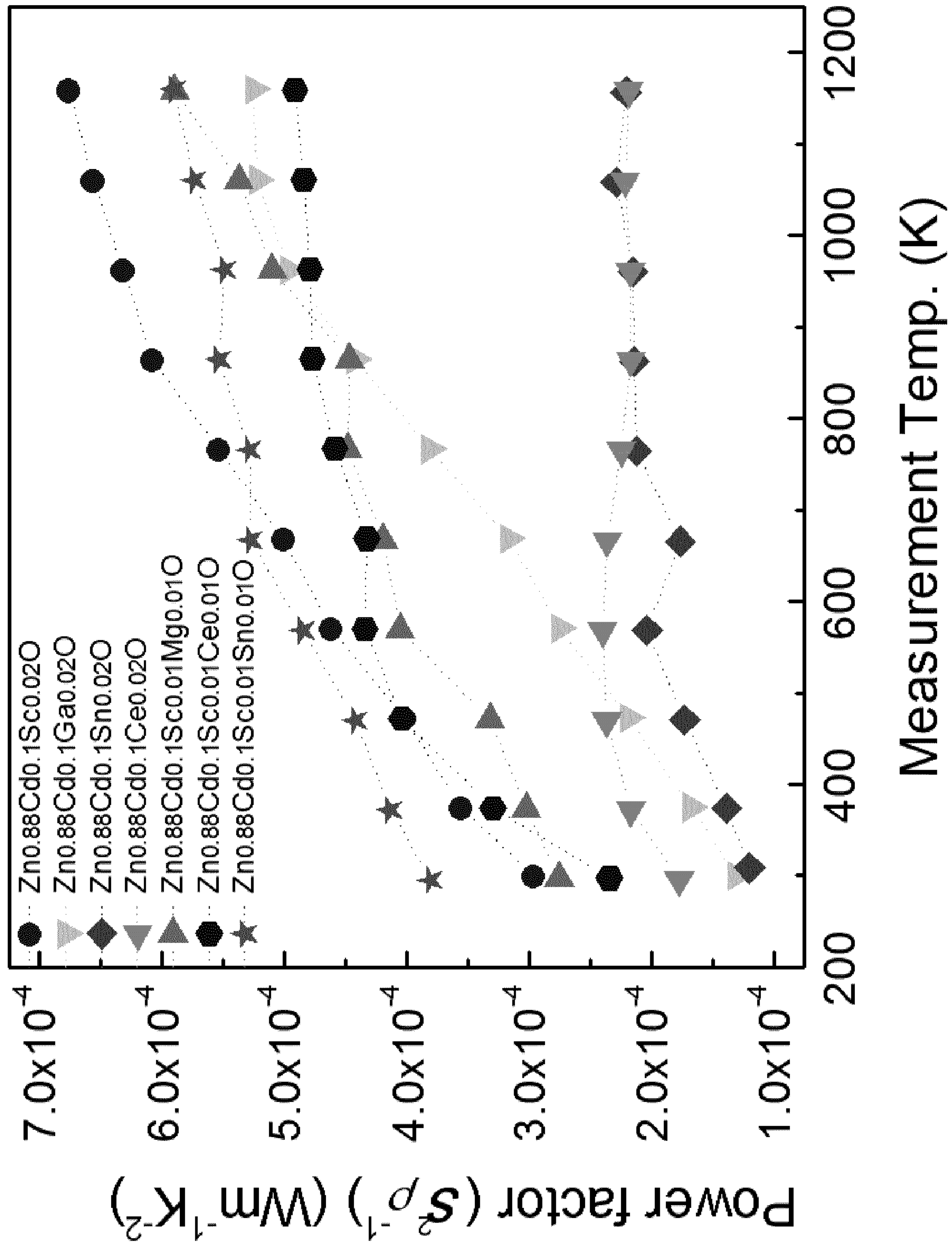

Zn0.88Cd0.1Sc0.02O
Zn0.88Cd0.1Ga0.02O
Zn0.88Cd0.1Sn0.02O
Zn0.88Cd0.1Ce0.02O
Zn0.88Cd0.1Sc0.01Mg0.01O
Zn0.88Cd0.1Sc0.01Ce0.01O
Zn0.88Cd0.1Sc0.01Sn0.01O
Power factor ($S^2\rho^{-1}$) ($Wm^{-1}K^{-2}$)
7.0x10^{-4}
6.0x10^{-4}
5.0x10^{-4}
4.0x10^{-4}
3.0x10^{-4}
2.0x10^{-4}
1.0x10^{-4}
200
400
600
800
1000
1200
Measurement Temp. (K)

FIG. 7C

FIG. 8A

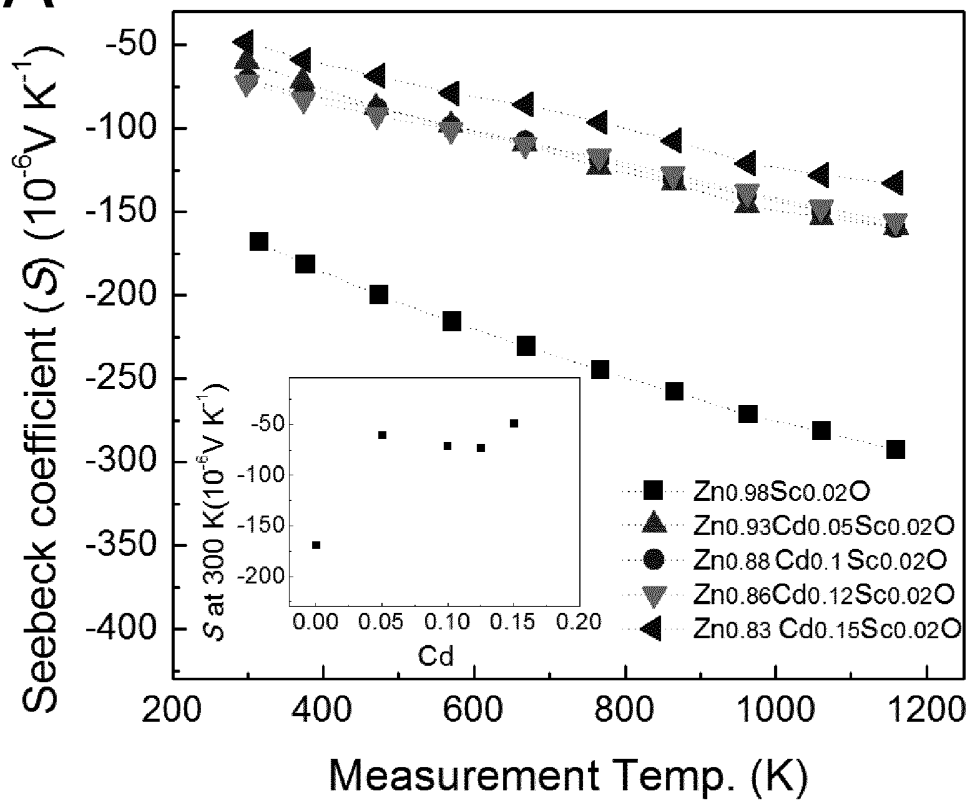

Seebeck coefficient (S) (10^-6 V K^-1)
Measurement Temp. (K)
S at 300 K(10^-6 V K^-1)
Cd
Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88 Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83 Cd0.15Sc0.02O

FIG. 8B

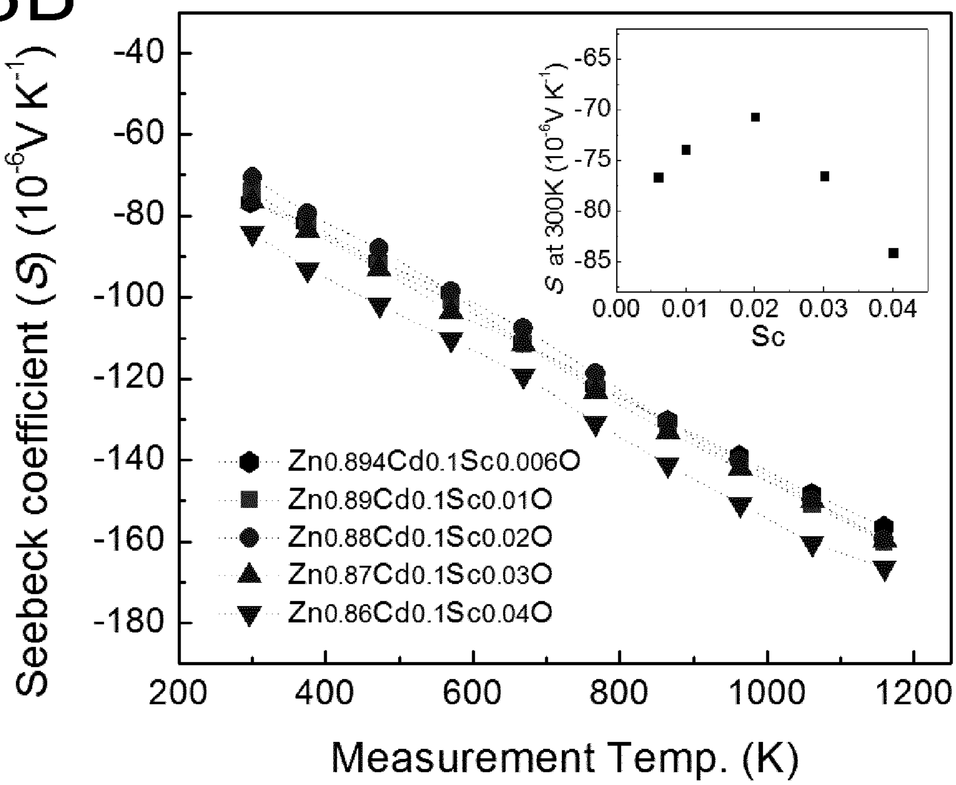

Seebeck coefficient (S) (10^-6 V K^-1)
Measurement Temp. (K)
S at 300K (10^-6 V K^-1)
Sc
Zn0.894Cd0.1Sc0.006O
Zn0.89Cd0.1Sc0.01O
Zn0.88Cd0.1Sc0.02O
Zn0.87Cd0.1Sc0.03O
Zn0.86Cd0.1Sc0.04O

FIG. 9A

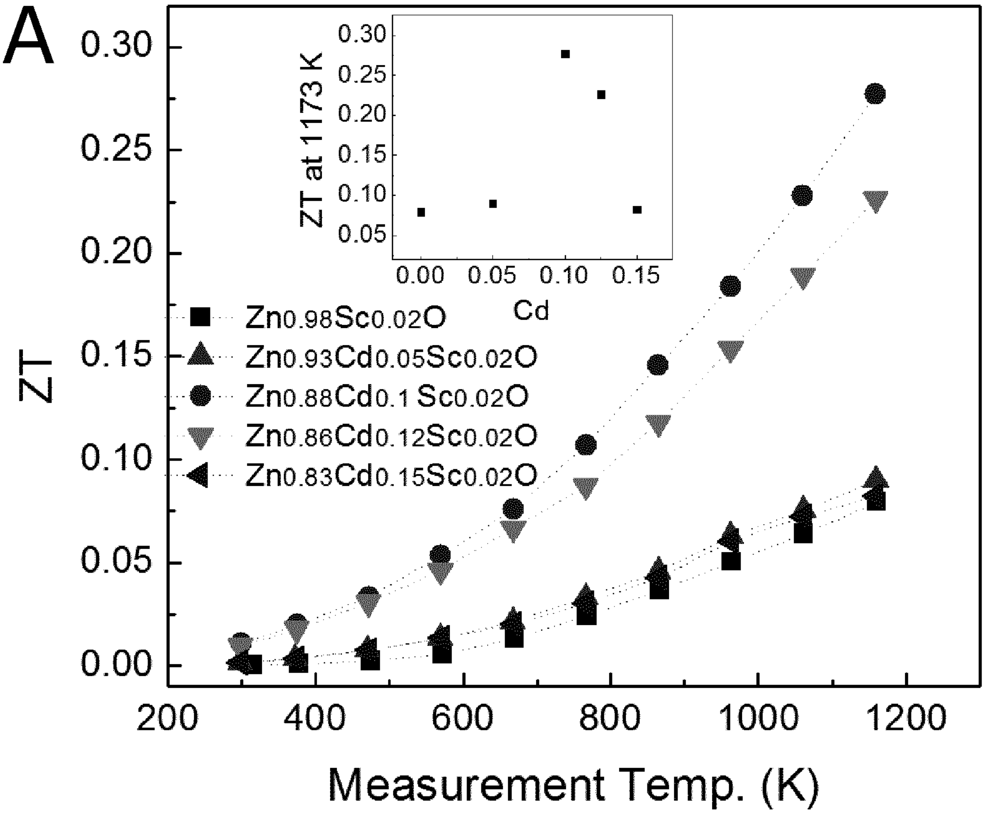
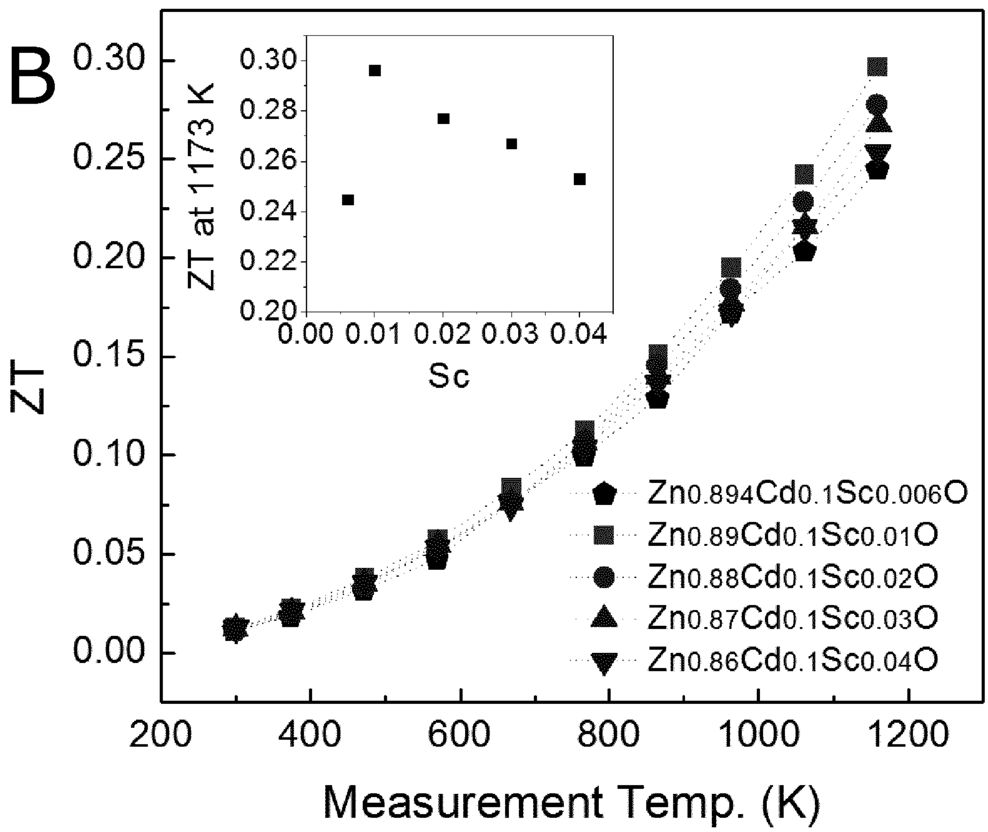

ZT
Measurement Temp. (K)
ZT at 1173 K
Cd
Zn0.98Sc0.02O
Zn0.93Cd0.05Sc0.02O
Zn0.88Cd0.1 Sc0.02O
Zn0.86Cd0.12Sc0.02O
Zn0.83Cd0.15Sc0.02O

FIG. 9B


ZT
Measurement Temp. (K)
ZT at 1173 K
Sc
Zn0.894Cd0.1Sc0.006O
Zn0.89Cd0.1Sc0.01O
Zn0.88Cd0.1Sc0.02O
Zn0.87Cd0.1Sc0.03O
Zn0.86Cd0.1Sc0.04O

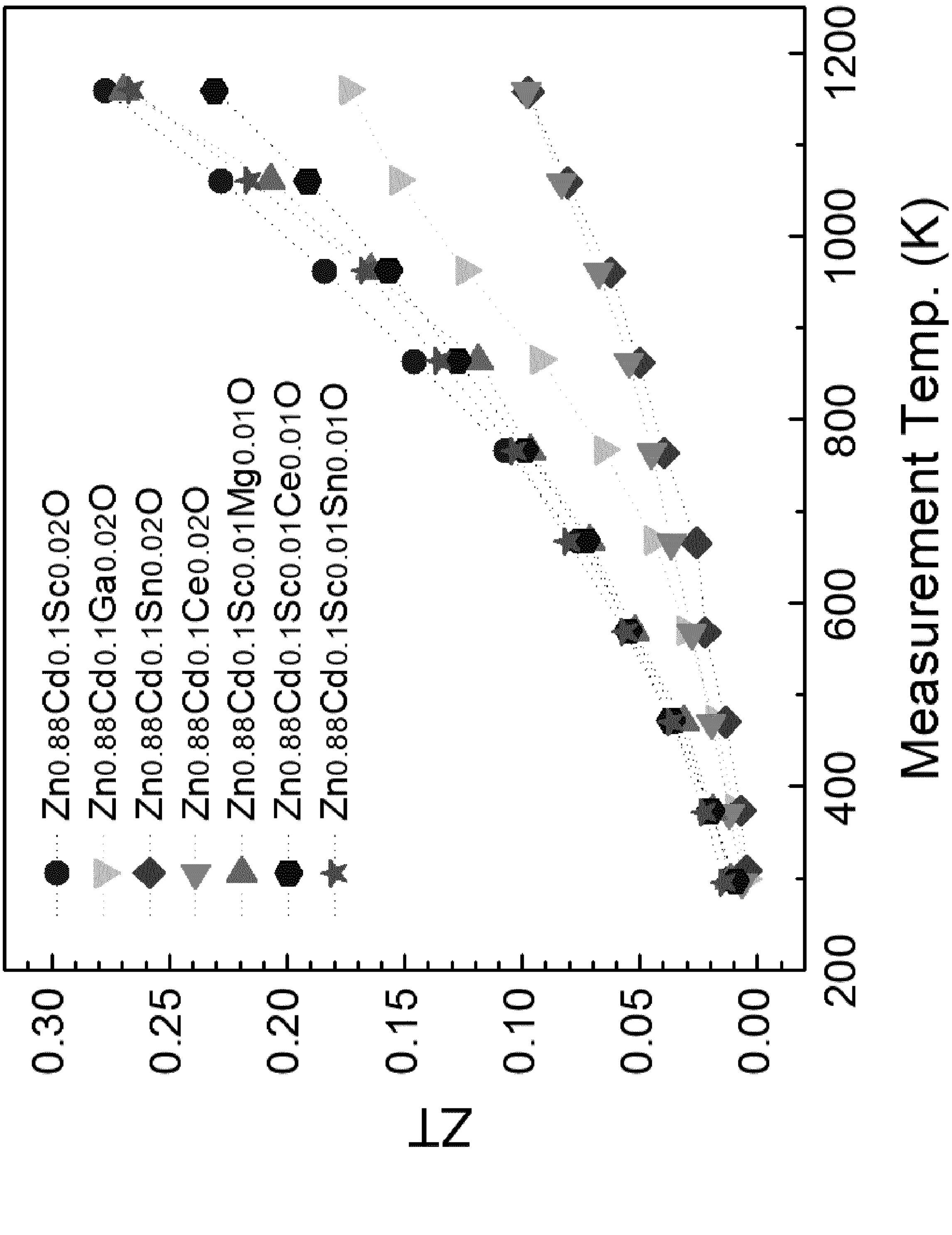

$Zn_{0.88}Cd_{0.1}Sc_{0.02}O$
$Zn_{0.88}Cd_{0.1}Ga_{0.02}O$
$Zn_{0.88}Cd_{0.1}Sn_{0.02}O$
$Zn_{0.88}Cd_{0.1}Ce_{0.02}O$
$Zn_{0.88}Cd_{0.1}Sc_{0.01}Mg_{0.01}O$
$Zn_{0.88}Cd_{0.1}Sc_{0.01}Ce_{0.01}O$
$Zn_{0.88}Cd_{0.1}Sc_{0.01}Sn_{0.01}O$
ZT
0.30
0.25
0.20
0.15
0.10
0.05
0.00
200
400
600
800
1000
1200
Measurement Temp. (K)

FIG. 10

FIG. 11A

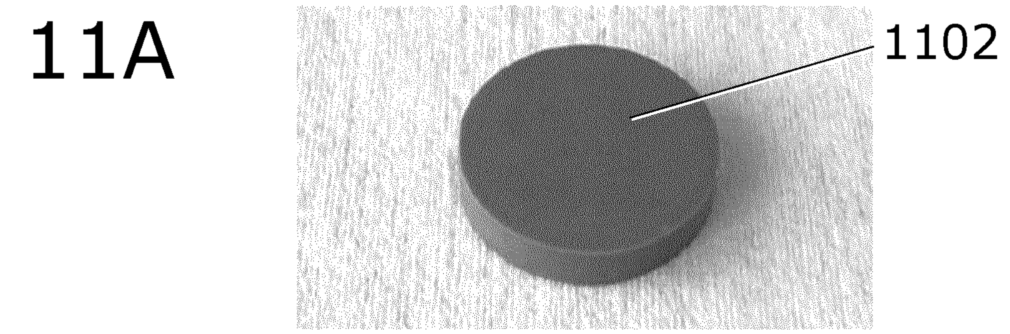


FIG. 11B

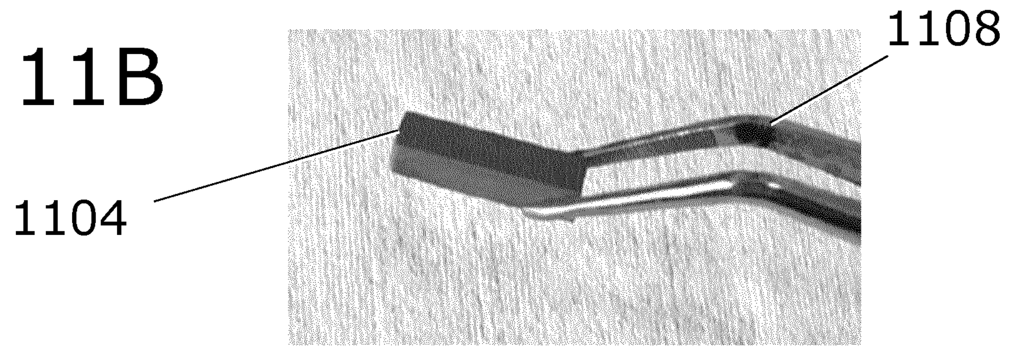


FIG. 11C

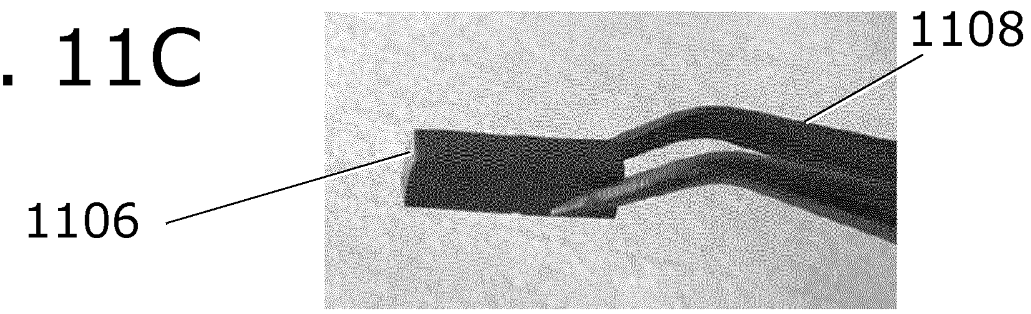


FIG. 12

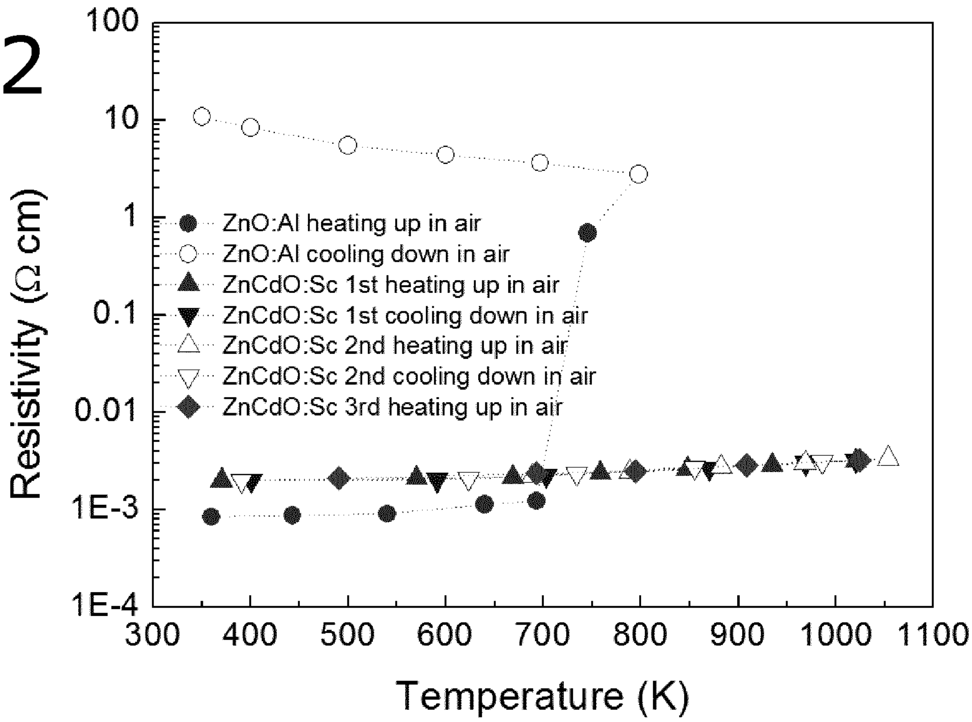

100
10
1
0.1
0.01
1E-3
1E-4
Resistivity (Ω cm)
300 400 500 600 700 800 900 1000 1100
Temperature (K)
ZnO:Al heating up in air
ZnO:Al cooling down in air
ZnCdO:Sc 1st heating up in air
ZnCdO:Sc 1st cooling down in air
ZnCdO:Sc 2nd heating up in air
ZnCdO:Sc 2nd cooling down in air
ZnCdO:Sc 3rd heating up in air

FIG. 13

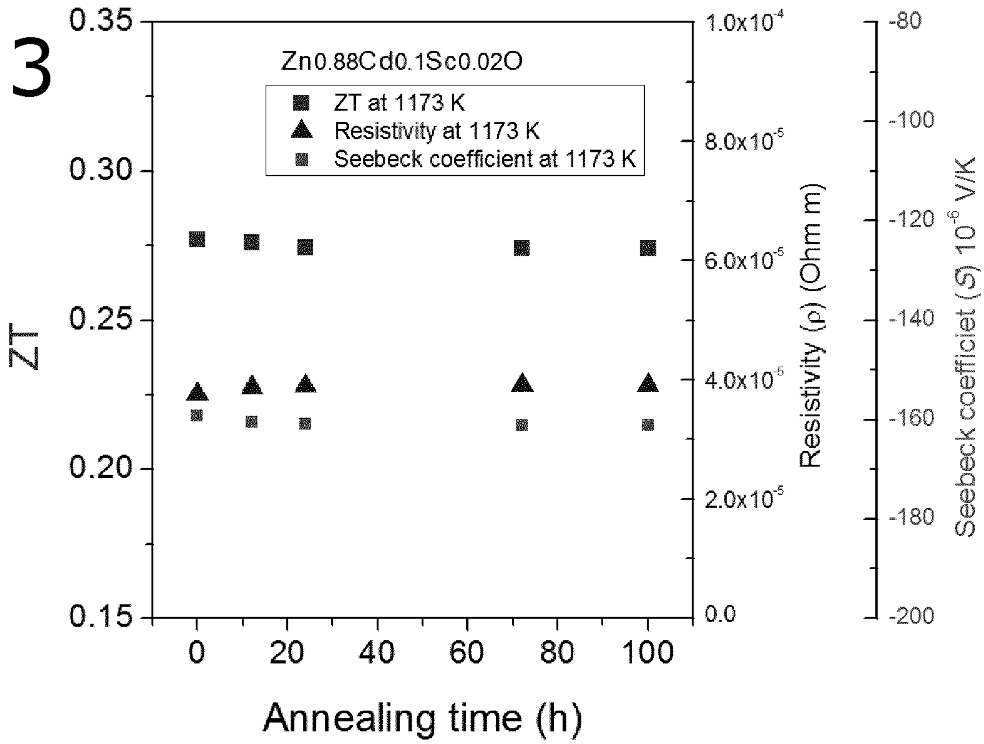

Zn0.88Cd0.1Sc0.02O
ZT at 1173 K
Resistivity at 1173 K
Seebeck coefficient at 1173 K
ZT
0.35 0.30 0.25 0.20 0.15
Resistivity (ρ) (Ohm m)
1.0x10^-4 8.0x10^-5 6.0x10^-5 4.0x10^-5 2.0x10^-5 0.0
Seebeck coefficiet (S) 10^-6 V/K
-80 -100 -120 -140 -160 -180 -200
0 20 40 60 80 100
Annealing time (h)

FIG. 14

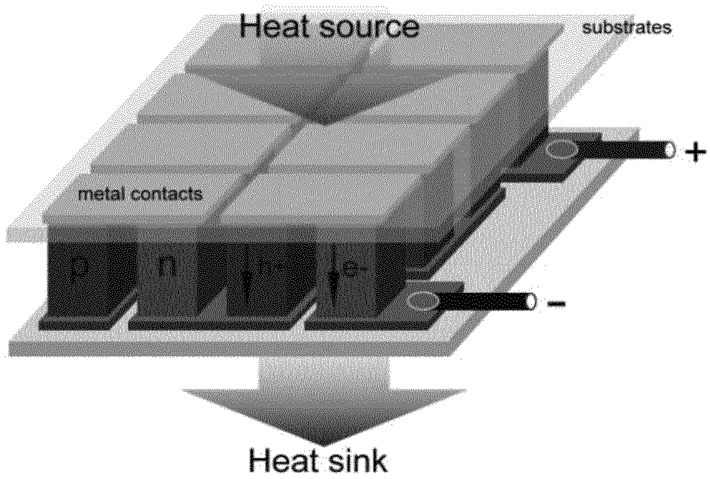


FIG. 15A

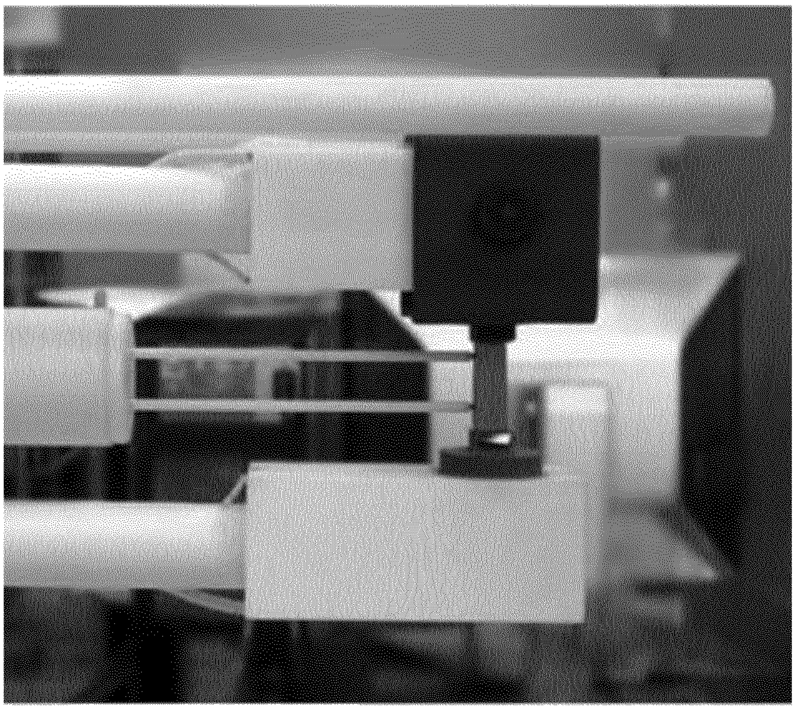
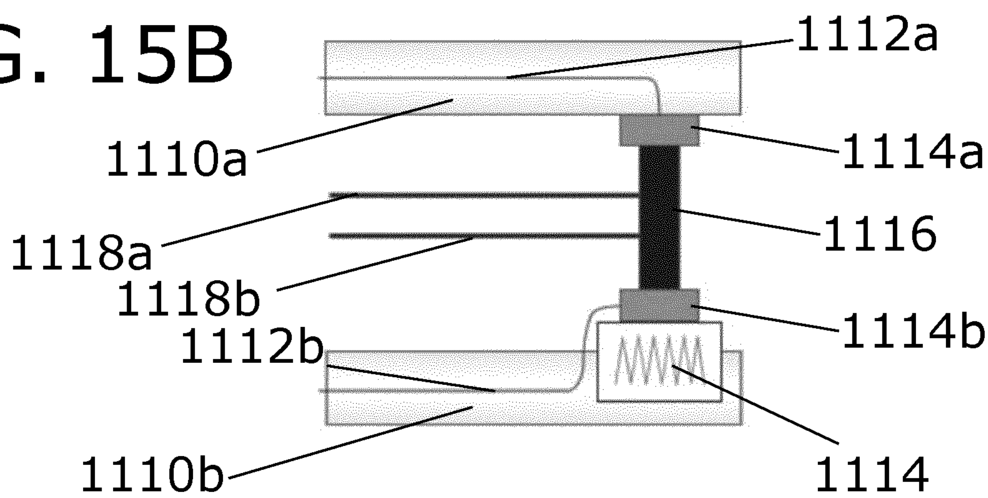


FIG. 15B



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/072492

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G9/00 C01G9/02 C01G11/00 H01L35/22
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/114172 A1 (TOTO LTD [JP]; TOKUDOME HIROMASA [JP]) 7 October 2010 (2010-10-07) Comparative example 1 claims	1-15
A	HIROYUKI YAMAGUCHI ET AL: "Thermoelectric Properties of ZnO Ceramics Co-Doped with Al and Transition Metals", JOURNAL OF ELECTRONIC MATERIALS, vol. 40, no. 5, 8 February 2011 (2011-02-08), pages 723-727, XP055184726, ISSN: 0361-5235, DOI: 10.1007/s11664-011-1529-9 page 724 "Experimental procedures"	1-15

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 November 2015	02/12/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Besana, Sonia

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YAMINI SHARMA ET AL: "Study of electronic and optical properties of Sc-, Y-, Ti-doped transparent conducting oxide", INDIAN JOURNAL OF PURE & APPLIED PHYSICS, vol. 49, 1 September 2011 (2011-09-01), pages 619-626, XP055184778, abstract -----	1-15
A	YASEMIN CAGLAR ET AL: "Morphological, optical and electrical properties of CdZnO films prepared by sol-gel method", JOURNAL OF PHYSICS D: APPLIED PHYSICS, INSTITUTE OF PHYSICS PUBLISHING LTD, GB, vol. 42, no. 6, 21 March 2009 (2009-03-21), page 65421, XP020149363, ISSN: 0022-3727, DOI: 10.1088/0022-3727/42/6/065421 abstract -----	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/072492

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010114172 A1	07-10-2010	JP 5660031 B2	28-01-2015
		WO 2010114172 A1	07-10-2010